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► **To cite this version:**

S. Rezgui, A. Amrane, F. Fourcade, A. Assadi, L. Monser, et al.. Electro-Fenton catalyzed with magnetic chitosan beads for the removal of Chlordimeform insecticide. *Applied Catalysis B: Environmental*, 2018, 226, pp.346-359. 10.1016/j.apcatb.2017.12.061 . hal-01695566

**HAL Id: hal-01695566**

**<https://univ-rennes.hal.science/hal-01695566>**

Submitted on 10 Sep 2018

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## Electro-Fenton catalyzed with magnetic chitosan beads for the removal of Chlordimeform insecticide

Soumaya Rezgui<sup>a,b,c\*</sup>, Abdeltif Amrane<sup>a</sup>, Florence Fourcade<sup>a</sup>, Aymen Assadi<sup>a</sup>, Lotfi Monser<sup>b,c</sup>, Nafaa Adhoum<sup>c</sup>

<sup>a</sup> *Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France.*

<sup>b</sup> *Institut National des Sciences Appliquées et de Technologie, B.P. N°676, 1080 Tunis Cedex, Tunisia.*

<sup>c</sup> *Unité de Recherche en Electrochimie, Matériaux et Environnement (UR16ES02), IPEIK, Université de Kairouan, Kairouan, Tunisia.*

\* *Corresponding author: Tel.: +216 54 331 379; fax: +216 71 704 329*

*E-mail address: [soumaya.rezgui@insat.rnu.tn](mailto:soumaya.rezgui@insat.rnu.tn)*

### Abstract

The degradation of chlordimeform (CDM) has been investigated by a heterogeneous electro-Fenton process involving magnetite supported chitosan beads (Fe<sub>3</sub>O<sub>4</sub>-Cs) as catalyst. The catalyst was prepared by dropwise addition of an acidic chitosan-metal salts solution into sodium hydroxide precipitation bath. SEM, XRD and FTIR analysis were used to characterize the catalysts. The effect of experimental parameters, such as the current intensity, the amount of iron on chitosan beads, the concentration of the catalyst and the initial pH on the pollutant removal rate was investigated. The optimal conditions for the degradation of 37.5 mg.L<sup>-1</sup> initial CDM concentration were achieved at an applied cathodic current of -5mA, using 0.5 g.L<sup>-1</sup> of magnetic chitosan beads (with an average iron amount of 0.104 mmol) and at pH=3. Under these conditions, CDM was effectively removed within 30 min with 80% of NPOC removal after 6 hours of treatment. The reaction followed a pseudo-first order kinetic equation. The adsorption test on the chitosan beads (with and without iron) demonstrated that the insecticide removal was solely induced by heterogeneous electro-Fenton treatment with Fe<sub>3</sub>O<sub>4</sub>-CS beads. In addition, the reusability of this catalyst was effectively demonstrated. Finally, LC-MS analysis allowed the proposal of a plausible degradation route.

**Key words:** Chlordimeform; magnetic chitosan beads; heterogeneous process; Electro-Fenton.



1 The hydrogen peroxide is produced in an aqueous medium by the reduction of dissolved  
2 oxygen by an electro-Fenton process (Eq.2).



4 Hence, the electro-Fenton solves the problems of transportation and storage of this compound,  
5 which is expensive, unstable and potentially harmful.

6 On the other hand, to avoid problems related to the loss of dissolved iron and the production  
7 of solid sludge, recent investigations focused on the possibility of using heterogeneous  
8 catalysts [27-31]. For this purpose, magnetite Fe<sub>3</sub>O<sub>4</sub> has attracted a great attention as efficient  
9 catalyst for the heterogeneous Fenton process due to its simple handling, ease of recovery  
10 with an external magnetic field, oxidative stability, biological compatibility, strong  
11 superparamagnetic behavior and its high catalytic activities [32-34]. The Fenton activity is  
12 due to the special structural characters of magnetite which has a cubic inverse spinel structure  
13 with tetrahedral and octahedral sites filled by Fe(II) and Fe(III) cations. The catalytic activity  
14 is mainly due to the octahedral cations which are almost exclusively exposed on the surface.  
15 The octahedral sites are occupied by both Fe(II) and Fe(III) , allowing the Fe species to be  
16 reversibly oxidized and reduced while keeping the same structure [35, 36]. However, the use  
17 of Fe<sub>3</sub>O<sub>4</sub> NPs can cause the problem of nanoparticles aggregation and the rapid degradation  
18 of magnetite onto a given biological matrix [37]. These problems can be overcome by  
19 preparation of a hybrid biocomposite using biopolymers as support.

20 Advantageous alternative supports including biopolymers and biomass-related polymers have  
21 been recently employed for the preparation of supported NPs. Biopolymers, such as chitosan  
22 and alginate, are indeed attractive candidates to be employed as supports for catalytic  
23 applications. They offer several advantages compared to traditional supports including low  
24 toxicity and cost, high biocompatibility, availability and abundance [38].

25  
26 In the last few years, chitosan (CS) has attracted researchers' attention as a natural chelating  
27 agent for use in chemical catalysts due to its strong affinity to transition metals, its high  
28 sorption capacity, stability of metal anions and physical and chemical versatility [39, 40].

29 The use of appropriate supports to avoid nanoparticles aggregation, as well as the production  
30 of supported nanoparticles with higher homogeneous dispersion remains a scientific challenge  
31 as attested by the numerous recent studies dealing with this subject [38, 41]. Therefore, the  
32 aim of this study was to develop highly homogeneous magnetic chitosan beads with a good  
33 catalytic activity and stability for CDM insecticide removal by the electro-Fenton process.

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## **2. Experimental set up**

### **2.1. Chemicals products**

All chemicals used were of analytical grade and used without further purification. Chlordimeform, sodium hydroxide (NaOH) and magnetite Iron (II,III) oxide  $\text{Fe}_3\text{O}_4$  were obtained from Sigma-Aldrich (France). Acetic acid was obtained from Acros Organics (France). Ferrous sulfate Iron (II) ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was purchased from Prolabo (France). Iron (III) chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and sodium sulfate decahydrate were from Acros Organics. Sulfuric acid and nitric acid were supplied by Carlo Erba. acetonitrile (HPLC-grade) was purchased from Fisher Scientific (Loughborough, UK). Ultra-pure water obtained from ELGA Purelab Option-Q DV 25 system was utilized for the preparation of all working solutions, as well as HPLC and LC– MS/MS mobile phases.

### **2.2. Electrochemical process**

The electrochemical heterogeneous Fenton reaction was performed in an undivided closed glass cell. The EF process was conducted in galvanostatic mode. The applied current was provided by a power supply Micolab Micronic System (Villetted’anthon, Fr), and the current was controlled and frequently regulated. The cathode was a carbon felt piece (1.5 cm length, 1 cm width, 0.5 cm thickness) and the anode was a platinum wire. The hydrogen peroxide  $\text{H}_2\text{O}_2$  was produced electrochemically by continuously bubbling compressed air near the cathode leading to the reduction of dissolved oxygen (DO) in acidic solutions containing dilute supporting electrolyte. The pH was adjusted by addition of dilute solutions of sulfuric acid or sodium hydroxide. The ionic strength was maintained constant by the addition of an inert supporting electrolyte (0.05 M,  $\text{Na}_2\text{SO}_4$ ). Prior to the electrolysis, compressed air was bubbled for 15 min through the aqueous solutions. Samples were regularly taken to measure the insecticide concentration.

### **2.3. Analytical procedures**

#### ***2.3.1. Non-purgeable organic carbon (NPOC) measurements***

The mineralization of the chlordimeform was monitored by measuring the non-purgeable organic carbon (NPOC) abatement by TOC-VCPH/CPN Total Organic Carbon Analyzer Schimadzu.

### 2.3.2. HPLC analysis

The measurements of the residual CDM concentration were performed by a Waters High Performance Liquid Chromatography (HPLC) system consisting of a Waters<sup>TM</sup> 600 instrument, equipped with a C18 reverse-phase Column (4.6 mm × 250 mm, 5 μm), along with a 996 Photodiode array detector and a Waters 717 plus Autosampler injector. The system was controlled through an Empower program. Prior to analysis, the samples had to be filtered through a 0.45 μm filter. The injection volume was set at 50 μL and an isocratic eluent Water/Acetonitrile (60/40) was pumped at a flow rate of 1 mL min<sup>-1</sup>. CDM had a retention time of 10 min under these conditions and many peaks of the byproducts appeared at lower retention times. Detection was performed with a photodiode array detector Waters 996 at 240 nm.

The detection and evolution of carboxylic acids was followed by an ion exclusion chromatography system Dionex DX120. A system equipped with a column Dionex AS11-HS (4 × 250 mm) coupled to a conductivity detector was used. Separation was achieved by a gradient elution composed of a mixture of potassium hydroxide (KOH) and water, as follows: 0-10 min (isocratic 10 mM); 10-25 min (gradient from 10 to 45 mM); 25-35 min (isocratic 45mM). Flow rate was adjusted to 1 mL min<sup>-1</sup>. The injection volume was set at 250 μL. The system was connected with an acquisition and data treatment unit commanded by analytical Chromeleon SE software.

The determination of inorganic anions was carried out by an ion chromatography system (IC-861, Metrohm) equipped with an AS4A-SC column (150 mm × 4 mm). The eluents were Na<sub>2</sub>CO<sub>3</sub> (3.2 mM) and NaHCO<sub>3</sub> (1 mM) solutions pumped at a flow rate of 0.7 mL min<sup>-1</sup> and a pressure of around 2000 psi.

### 2.3.3. UPLC-MS/MS analysis

The degradation intermediates were identified through LC-MS/MS ultra-high pressure liquid chromatography (Acquity UPLC – Waters) coupled to a Waters Micromass Quattro Premier (Waters Corporation, Manchester, UK) triple quadruple mass spectrometer as detector. It was operating with an electrospray source in positive ionization mode with a cone potential of 25 V. Analyses were performed in full scan and daughter scan modes, with a collision energy of 25 eV. Spectra were acquired between 80 and 500 m/z and the data were treated with Micromass Mass-Lynx 4.1 software. The UPLC system (Waters Corporation, Milford, MA,

1 USA) consists of an Acquity UPLC binary solvent manager, an Acquity UPLC sample  
2 manager and an Acquity UPLC column heater equipped with a Waters Acquity UPLC BEH  
3 Shield RP18 column (2.1 mm × 100 mm, 1.7 mm particle size) (Milford, MA, USA)  
4 maintained at 45 °C. Analyses were performed using 0.1% formic acid in acetonitrile as  
5 eluent A and 0.1% formic acid in a mixture of MilliQ Water/Acetonitrile (90/10, v/v) as  
6 eluent B, delivered at a flow rate of 0.4 mL min<sup>-1</sup>. The elution gradient started with 100% of  
7 eluent B. After 1 min, the proportion of eluent A increased linearly to 100% of A within 8  
8 min.

#### 9 **2.3.4. Determination of the iron content**

10 The amount of iron in the catalyst, as well as, the total leached iron was determined by atomic  
11 absorption spectrophotometry (AA140, VARIAN) whose detection limit is estimated to 3.1  
12 μmol.L<sup>-1</sup>. For the heterogeneous catalysts, it was necessary to obtain an iron solution by acid  
13 leaching samples of Fe<sub>3</sub>O<sub>4</sub>-Cs beads in concentrated hydrochloric acid solution until complete  
14 discoloration of the bead (after 12 hours).

15 In order to determine the molar ratio Fe<sup>2+</sup>/Fe<sup>3+</sup> in Fe<sub>3</sub>O<sub>4</sub>-Cs beads, soluble iron quantification  
16 was estimated by the standard 1,10-phenantroline spectrophotometric method [42]. 1,10-  
17 phenantroline reacted with Fe<sup>2+</sup> forming a colored complex which can be measured at a  
18 wavelength of 510 nm. While the amount of the individual Fe<sup>3+</sup> was calculated from the  
19 difference between the total iron and the Fe<sup>2+</sup>. The amount of total iron was estimated by the  
20 same spectrophotometric method after the addition of a reducing agent of Fe<sup>3+</sup> to Fe<sup>2+</sup>.

#### 21 **2.3.5. Determination of the zero point charge of the catalyst**

22 The pH of zero point charge pH<sub>zpc</sub> was determined by the simple method of salt addition [43].  
23 A series of 5 suspensions were prepared by mixing 40 mL of sodium nitrate NaNO<sub>3</sub> (0,1M)  
24 with 0.2 g of sample. The pH of each solution in the series of NaNO<sub>3</sub> was beforehand  
25 adjusted to 2, 6, 8, 10 and 12 using a diluted HNO<sub>3</sub> or NaOH solution. Then, each flask was  
26 vigorously agitated for 24h. The final pH was measured. After this time each resulting pH  
27 was measured and the initial pH (pH<sub>0</sub>) vs. the difference between the initial and final pH  
28 values (ΔpH) was plotted. The pH<sub>pzc</sub> was taken as the point where ΔpH = 0.

#### 29 **2.3.6. Morphology of the beads**

1 Surface morphology was characterized on a field-emission scanning electron microscope  
2 (SEM). SEM was performed on a field effect JEOL JSM-6301F instrument equipped with an  
3 EDS Oxford Inca Energy 300 SEM at an accelerating voltage of 15 kV.

#### 4 **2.3.7. FTIR and XRD analysis**

5 Catalysts and virgin chitosan beads were characterized using a FTIR model spectrum 100  
6 (PerkinElmer, USA) with a wavelength run of 4000-400 $\text{cm}^{-1}$ . For the same samples, XRD  
7 measurements were carried out using X'Pert PRO MPD X-ray diffractometer (PANalytical)  
8 with monochromatic Cu-K $\alpha$  radiation source ( $\lambda=1,5418 \text{ \AA}$ ).

### 9 **2.4. Preparation of magnetic chitosan beads**

10 The chitosan used in the current work was extracted from shrimp shell waste according to the  
11 preparation method detailed by Islam et al [44]. Shrimp shells were collected from the central  
12 market of Tunis.

#### 13 **2.4.1. One-step method for the preparation of magnetic chitosan gel beads (The in-situ 14 method)**

15 The in-situ formation of magnetic particles in polymer matrix can be obtained by the alkaline  
16 co-precipitation of ferric and ferrous salts [45]. For the synthesis of magnetic chitosan gel  
17 beads,  $\text{Fe}^{3+}:\text{Fe}^{2+}$  in the molar ratio 2:1 were added to 2% chitosan dissolved in acetic acid  
18 solution 1%. The gel solution was mixed by constant stirring for 1 hour to obtain an orange  
19 homogeneous gel solution. Then, the mixture was dropped through a syringe into a hardening  
20 solution of sodium hydroxide (1 M) to create spherical and uniform chitosan gel beads which  
21 have magnetic properties (Fig.2 and Fig.3). In contact with NaOH solution, the dark color of  
22 the beads indicates the in-situ precipitation of iron oxide. Nanoparticles of metal oxides, in  
23 particular, magnetite  $\text{Fe}_3\text{O}_4$  and maghemite  $\text{Fe}_2\text{O}_3$  are often synthesized by the alkaline co-  
24 precipitation of ferric and ferrous salts. [46].

25 The obtained particles were washed with deionized water for several times until pH reached a  
26 constant value ( $\approx 6$ ). Then, the prepared beads were dried at room temperature.

27 **Figure 2**

28 **Figure 3**

29



1 **2.4.2. Method 2: the mixing of pre-formed polymer and magnetic particles (The ex-situ**  
2 **method)**

3 For comparison, magnetic chitosan beads Fe<sub>3</sub>O<sub>4</sub>-Cs was prepared by deposition of magnetite  
4 (Fe<sub>3</sub>O<sub>4</sub>) at the surface of chitosan gel beads. Chitosan beads were prepared by the previously  
5 described method without the addition of iron. Thereafter, prepared particles were introduced  
6 into 1% magnetite suspension. The mixture was stirred for 12 hours using an incubator shaker  
7 (innova<sup>®</sup>40).

8 **3. Results and discussion**

9 **3.1. Structural and textural characterization of the catalyst**

10 **3.1.1. Principle of in-situ preparation of magnetite nanoparticles in chitosan matrix**

11 The main advantage of the in-situ approach is the synthesis of the nanosized magnetite and  
12 the solidification of chitosan beads in the alkaline co-precipitation bath. This occurs in one  
13 step and can be described according to the following reaction:



15 As explained by Wang [47], ferric and ferrous ions are chelated by amino groups of chitosan  
16 in the prepared mixture CS/iron salts gel solution. Then, in contact with hydroxide ions the  
17 chelated ferrous and ferric ions [(chitosan-NH<sub>2</sub>)<sub>2</sub>-Fe<sup>2+</sup>, (chitosan-NH<sub>2</sub>)<sub>2</sub>-Fe<sup>3+</sup>] provide  
18 nucleation site for magnetite crystals. Thus, Fe<sub>3</sub>O<sub>4</sub> and chitosan would be precipitated at the  
19 same time. The scheme of the in-situ preparation principle of magnetite in chitosan matrix is  
20 presented in **Figure 4**.

21 This way of preparation is more advantageous than that involving magnetite powder,  
22 since it allows a better homogenization of the solution and thus minimizes the loss of  
23 magnetic material during the preparation procedure [48]. The homogeneous  
24 distribution of metal oxide in the catalyst is due to the uniform distribution of amino  
25 groups in the chitosan matrix. Therefore, formed metal nanoparticles are strongly bound to  
26 chitosan by combination with a wide number of active sites of the polymer [49]. In fact, in the  
27 in-situ approach, the polymer is involved in the synthesis of metal oxide nanoparticles; it has  
28 therefore a positive impact on their stabilization and their isolation reduces the problem of  
29 aggregation. This can enhance the catalytic performance of prepared magnetic chitosan beads.  
30 To highlight the effect of iron concentration on the textural properties of the catalyst, the  
31 amount of iron added to chitosan gel solution (2%) was varied from 5 to 15mmol per 1 g of  
32 chitosan flakes. The obtained catalysts were characterized by SEM image, XRD and FTIR  
33 analysis.

## Figure 4

### 3.1.2. Morphology and bead size measurements

For the in-situ approach, the morphology of the beads surface and the core observed by SEM micrographs (Fig.5) after drying demonstrated that, for high concentrations of iron ( $\geq 10$  mmol of iron/1g of CS) (Fig.5.a and Fig.5.b), beads have an elongated spherical form with a rather smooth surface. For a low concentration of iron (=5 mmol of iron/1g of CS) (Fig.5.c), the bead loses its spherical shape and its surface became crumpled.

For these catalysts, wet beads had a spherical form. After drying, beads with a high amount of iron retained their spherical shape. In contrast, beads with a low amount of iron showed an empty pocket structure similar to that found by Xiaopeng Xiong et al who explained this result by the shrinkage of the particles by removal of the inside water during drying [50].

Besides, the difference between the surface of chitosan without and with the deposit of  $\text{Fe}_3\text{O}_4$  nanoparticles was obvious in Fig 5.d and Fig 5.e respectively; magnetite particles are visible on the surface of  $\text{Fe}_3\text{O}_4$ -Cs beads prepared by the ex-situ approach.

## Figure 5

The dried bead size was measured by laser diffractometry using (Mictotrac-S3500) considering the MIE and FRAUNHOFER theory (0.02 microns to 2800 microns). For all  $\text{Fe}_3\text{O}_4$ -Cs beads prepared via the in-situ approach, the diameter is still constant, and it is estimated to around 1.3 mm (Fig.3.d). Therefore, the size of beads is not affected by the amount of iron salts added initially to the chitosan gel matrix.

### 3.1.3. Phase structure of the catalysts

The presence of magnetite ( $\text{Fe}_3\text{O}_4$ ) phase was confirmed by XRD analysis of dried CS/ $\text{Fe}_3\text{O}_4$  beads (in situ synthesis) (Fig.6). The iron oxide phase was identified from the XRD patterns by the peak positions at  $2\Theta = 30.4^\circ, 35.7^\circ, 43.5^\circ, 53.4^\circ, 57.4^\circ, 63.1^\circ$  and  $73.0^\circ$ , which can be attributed to the diffraction planes of (220), (311), (400), (422), (511), (440), (533), respectively, for the crystallized structure of the  $\text{Fe}_3\text{O}_4$ .

The mean size of the ferromagnetic particles, prepared in-situ in the beads was 10.2 nm, as calculated by the Scherrer's equation (Eq.4).

$$D = \frac{K \times \lambda}{\beta \times \cos(\Theta)} \quad \text{Eq. 4}$$

1 Where D is the mean size of crystallites (nm), K is a constant related to crystallite shape,  
2 normally taken as 0.9,  $\lambda$  is the X-ray wavelength,  $\beta$  is the full width at half the maximum  
3 (radians) of the X-ray diffraction peak and  $\theta$  is the Bragg angle (deg).

4 This finding is in agreement with the related literature [51]; the Fe<sub>3</sub>O<sub>4</sub> crystals induced by the  
5 chitosan hydrogel should have a narrow size distribution and a small diameter due to the  
6 restriction of iron ions by the chelation effect that avoids the crystal growth of magnetite. It  
7 has been reported that Fe<sub>3</sub>O<sub>4</sub> particles with size lower than 20 nm are superparamagnetic [46].  
8 Therefore, it might be assumed that a part of the magnetite, formed *in situ* in the beads, was in  
9 a superparamagnetic state. It means that they are easily attracted by a magnetic field, but  
10 retain no residual magnetism at zero magnetic field [52]. The superparamagnetism is an  
11 important advantage which provided an additional stability of our catalyst and its dispersion  
12 after the application of an external magnetic field.

13 Furthermore, the size of Fe<sub>3</sub>O<sub>4</sub> particles in the magnetic chitosan beads prepared by the ex-  
14 situ method was estimated to be 45.3 nm.

15

16

### Figure 6

#### 17 3.1.4. FTIR analysis of the catalysts

18 The deacetylation degree of the prepared chitosan (% DD) was estimated at around 75% and  
19 it was evaluated using the equation 5 proposed by Brugnerotto et al [53].

$$20 \quad \%DD = 100 - [[31.92*(A_{1320}/A_{1420})]-12.20] \quad \text{Eq.5}$$

21 Where A<sub>1320</sub> and A<sub>1420</sub> are the values of absorbance relative to baseline that occur in the FTIR  
22 spectrum of the extracted chitosan (Fig.7).

23 The binding of Fe<sub>3</sub>O<sub>4</sub> to chitosan and the effect of the amount of iron in the chitosan matrix  
24 were also confirmed by FT-IR analysis. Figure 7 shows the FT-IR spectra of prepared  
25 catalysts and virgin chitosan powders. In the FT-IR spectra of chitosan, the characteristic  
26 bands of NH- and OH- stretching vibrations appeared at 3430 cm<sup>-1</sup>. The band at 1645 cm<sup>-1</sup>  
27 was attributed to NH bending vibrations. The bands at 1150 cm<sup>-1</sup> (-OH bending), 1072 cm<sup>-1</sup> (-  
28 C-O-C- stretching vibrations) and 1031 cm<sup>-1</sup> (-OH bending) were due to the saccharide  
29 structure [48].

30 In the FT-IR spectra of the catalysts, a new band appeared in the low-frequency region (1000-  
31 500 cm<sup>-1</sup>) due to the iron oxide skeleton (-Fe-O- stretching vibration) which confirmed that  
32 the precipitation reactions carried out with chitosan produced a composite chitosan-Fe oxide

1 nanoparticles [48, 54, 55]. By increasing the amount of iron per mass of chitosan, the  
2 characteristic band of Fe-O became wide. Compared with the spectrum of chitosan, a slight  
3 shift and a significant decrease in the transmittance of the band at  $3430\text{ cm}^{-1}$  occurred  
4 following iron addition. This indicated the occurrence of metal-NH<sub>2</sub> bonds [56, 57].

## 6 **Figure 7**

### 7 **3.2. Degradation of chlordimeform by heterogeneous electro-Fenton process**

#### 8 **3.2.1. Effect of the current intensity**

9 A key parameter in the electro-Fenton process is the applied current in two-electrode cells  
10 [58-60]. Zhimin Qiang et al.[60] investigated the optimal parameters such as the cathodic  
11 potential to improve the Faradic current efficiency of H<sub>2</sub>O<sub>2</sub> production. They found that the  
12 optimal conditions for H<sub>2</sub>O<sub>2</sub> generation are cathodic potential of  $-0.5\text{V}$  vs. saturated calomel  
13 electrode (SCE), with an oxygen mass flow rate of  $8.2 \times 10^{-2}$  mol/min in acidic conditions. In  
14 this context, an electrochemical study carried out previously, in our working conditions (data  
15 not shown), indicated that  $-5\text{ mA}$  corresponded to an average current intensity obtained during  
16 electrolysis carried out at a constant potential of  $-0.5\text{ V/EDS}$ .

17 To confirm the effect of the current intensity on the electrochemical generation of H<sub>2</sub>O<sub>2</sub> with  
18 the felt carbon cathode, electrolysis was performed in our experimental conditions (30 mL of  
19 a  $0.05\text{ M Na}_2\text{SO}_4$  solution adjusted to an initial  $\text{pH}=3$  with concentrated H<sub>2</sub>SO<sub>4</sub>) by applying  
20 several cathodic current intensities. **Figure 8** shows the effect of the applied current intensity  
21 on the amount of accumulated hydrogen peroxide during 4 hours of electrolysis. The  
22 hydrogen peroxide concentration was measured by titration with a solution of potassium  
23 permanganate KMnO<sub>4</sub>. As expected, the measured concentration of the oxidant depends on  
24 the applied intensity. Final solutions with  $18.1 \pm 0.7$ ,  $20.7 \pm 0.2$ ,  $25.6 \pm 0.6$  and  $28.2 \pm 0.5\text{ mM}$   
25 hydrogen peroxide were obtained, after 4 hours of electrolysis, at  $-30$ ,  $-20$ ,  $-10$  and  $-5\text{ mA}$ ,  
26 respectively. Thus, the maximum hydrogen peroxide concentration was achieved at an  
27 applied cathodic current of  $-5\text{ mA}$ .

28 Taking into account that the degradation of CDM occurs by the reaction with hydroxyl  
29 radicals  $\bullet\text{OH}$  produced by the activation of the electro-generated hydrogen peroxide on the  
30 active sites of iron supported on chitosan beads, the rate of pollutant mineralization is  
31 directly affected by the amount of electro-generated hydrogen peroxide which is the precursor  
32 of this reaction.

1 These results are confirmed by the study of the impact of the current intensity on the CDM  
2 removal. To this purpose, various current intensities were applied, in the range of -5mA to -30  
3 mA. Results in **Fig.9.a** show that changing the applied cathodic current did not lead to a  
4 significant increase in the kinetic of degradation of CDM. However, it is clear from **Fig.9.b**  
5 that the change of the applied cathodic current greatly influenced the rate of mineralization  
6 because the values of NPOC removal within 4 hours of electrolysis decreased from  
7  $51.2\pm 4.5\%$  to  $14.9\pm 0.5\%$  for decreasing currents values from -5 mA to -30 mA. For higher  
8 current intensity, the NPOC removal decreased to  $29.5\pm 0.2\%$  for a cathodic current intensity  
9 equal to -2.5 mA. In the absence of catalyst, the yields of NPOC removal did not exceed  
10  $15.6\pm 1.3\%$  and  $5.7\pm 1.9\%$  for  $I=-5$  mA and  $I=-10$  mA, respectively.

11 From our study, the highest NPOC removal was obtained at an applied current equal to -5  
12 mA, which represents, as discussed above, the optimal applied current for the electro-  
13 generation of oxidant species. An applied cathodic current of -5mA was therefore selected  
14 and considered thereafter.

15 To highlight the contribution of the adsorption process on the removal of the insecticide, the  
16 catalyst was introduced into CDM solutions in the absence of current. Results showed that the  
17 fraction of CDM adsorbed in magnetic chitosan beads did not exceed 3%. This proves that  
18 there was no affinity between the target molecule and the catalyst. This result can be  
19 explained by the point of zero charge (pzc) value of the  $\text{Fe}_3\text{O}_4\text{-Cs}$  beads which is around  
20  $\text{pH}=7$  (**Table 1**). Thus, the catalyst surface is positively charged in acidic media ( $\text{pH} < 7$ ),  
21 whereas it is negatively charged under alkaline conditions ( $\text{pH} > 7$ ). At  $\text{pH}=3$ , the charge of  
22 catalyst surface is positive. However, the charge of CDM ( $\text{pKa}=3.85$ ) is neutral. This  
23 accounts for the weak interaction between the pollutant and the catalyst as proved by the  
24 adsorption test.

25 **Figure 8**

26 **Figure 9**

### 27 **3.2.2. Effect of the amount of iron in chitosan beads**

28 The catalytic activity is influenced by the availability of active sites (iron) on the surface of  
29 the catalyst which react, as mentioned previously, with hydrogen peroxide in order to  
30 generate hydroxyl radicals [29]. To highlight the effect of the iron content on the catalytic  
31 properties of magnetic chitosan beads, the amount of iron added initially to the chitosan  
32 matrix was varied from 5 to 15 mmol per 1 gram of polymer flakes. Iron analysis was carried  
33 out by atomic absorption spectroscopy to quantify the amount of metal/mass of catalyst for

1 each sample. The corresponding results are shown in **Table.1**. It can be noted that for the  
2 higher iron content (>15 mmol of iron/1 g of chitosan), the rigidity of the beads decreased;  
3 they could be easily broken by simple magnetic stirring.

4 **Fig.10** shows the time-courses of CDM removal during the electro-Fenton reaction. It can be  
5 seen that the kinetics of pollutant removal increased with increasing iron concentration and  
6 total removal was observed within 60 min as shown in **Fig.10.b**. The removal of the pesticide  
7 was found to follow a pseudo-first order kinetic model with  $k=0.072 \text{ min}^{-1}$ ,  $0.110 \text{ min}^{-1}$  and  
8  $0.160 \text{ min}^{-1}$  for 0.046 mmol, 0.083 mmol and 0.104 mmol of iron per 15 mg of catalyst,  
9 respectively. The mineralization yields (**Table 2**) also increased with the mass of iron, from  
10  $61.4\pm 2.1\%$  to  $79.7\pm 1.7\%$ , for amounts of iron per mass of chitosan increasing from 0.046  
11 mmol to 0.104 mmol, after 6 h of treatment.

12 To better understand the effect of the amount of iron on the structural and textural properties  
13 of magnetic chitosan beads, XRD and FTIR analysis and SEM micrographs were done.

14 From the diffractogram XRD (**Fig.6**), it can be concluded that the catalytic activity increased  
15 for higher crystalline structure. However, the crystallinity is a necessary but not the only  
16 important factor affecting the catalytic performance. The activity of catalyst is also affected  
17 by surface area and the porosity, which could be related to the increase of the amount of  
18 active sites available for the reaction. Thus, the highest amount (0.104 mmol) was selected as  
19 the optimal amount of iron supported on chitosan beads, ensuring a good stability of the  
20 catalyst and a high catalytic activity; it was therefore considered thereafter. As observed  
21 above, negligible involvement of pesticide adsorption on the chitosan beads, containing iron  
22 or not, was confirmed.

23 **Table 1**

24 **Figure 10**

25 **Table 2**

### 26 **3.2.3. Effect of the catalyst dosage**

27 In heterogeneous systems, the catalyst dosage plays a crucial role since it controls the rate of  
28 hydroxyl radicals' production. Thus, it is one of the major parameters to be studied. For this  
29 purpose, several experiments were performed with  $0.25 \text{ g.L}^{-1}$ ,  $0.5 \text{ g.L}^{-1}$  and  $0.75 \text{ g.L}^{-1}$  of  
30 catalyst.

1 As can be seen when the catalyst dosage increased from 0.25 g.L<sup>-1</sup> to 0.5 g.L<sup>-1</sup>, the percentage  
2 of degradation of CDM increased within 30 min from 65.5±2.2% to 99.1±0.9% (**Fig.11**), and  
3 the rate of NPOC removal after 6 hours of treatment increased from 63.5±0.8% to 79.7±1.7%  
4 respectively (**Table2**), because increasing the accessibility of iron led to an increase of  
5 catalytic active sites. However, beyond 0.5 g.L<sup>-1</sup> of catalyst, the CDM removal and the  
6 mineralization yields decreased to 82.6±4.2% (**Fig.11**) and 71.8±1.3% (**Table2**), respectively.  
7 This can be explained by the reaction of hydroxyl radicals with the excess of active iron sites  
8 as shown in **Eq.6**.



10 Otherwise, it has been reported that the increase of the catalyst dosage, may reduce the current  
11 intensity [**28**]. In fact, as commonly known, the mass of catalyst can greatly affect the mass  
12 transport in the medium which reduce the current intensity.

13 The degradation of CDM, with the change of catalyst concentration, followed a pseudo first  
14 order kinetic as shown in **Fig.11.b**, as found previously in **Fig.10.b**. The kinetic constants  
15 were found to be 0.042 min<sup>-1</sup>, 0.160 min<sup>-1</sup> and 0.057 min<sup>-1</sup> for 0.25 g.L<sup>-1</sup>, 0.5 g.L<sup>-1</sup> and 0.75  
16 g.L<sup>-1</sup>, respectively.

17 From the above results, 0.5 g.L<sup>-1</sup> was the optimal catalyst amount and was therefore  
18 considered thereafter.

### 19 **Figure 11**

#### 20 **3.2.4. Comparison of the different preparation methods of Fe<sub>3</sub>O<sub>4</sub>-CS beads**

21 Among the classical synthesis methods, detailed by White et al. [**38**] for the chemical  
22 preparation of supported metal nanoparticles on porous materials, two different methods  
23 were compared in the present study: The first was the synthesis in situ of the Fe<sub>3</sub>O<sub>4</sub> on a  
24 polymer matrix by the co-precipitation method; for comparison, the second method was a  
25 simple deposition of Fe<sub>3</sub>O<sub>4</sub> nanoparticles on pre-formed chitosan gel beads surface.

26 The Fe<sub>3</sub>O<sub>4</sub>-Cs beads prepared by the co-precipitation method were found to have a higher  
27 catalytic activity: it was observed 99.1±0.9% and 85.4±0.6% CDM removal within 30 min  
28 (**Fig.12**) and 79.7±1.7% and 37.8±2.3% mineralization after 6 hours (**Table 2**) of electrolysis  
29 by the methods 1 and 2, respectively. The first method allowed the incorporation of a  
30 considerable amount of magnetite in the beads (0.1039±0.0014 mmol of iron/ mass of

1 catalyst) with higher homogeneous dispersion compared to the deposition method of  
2 magnetite at the surface of chitosan beads. Indeed, the amount of iron deposited at the surface  
3 of Fe<sub>3</sub>O<sub>4</sub>-Cs beads prepared via the ex-situ approach was estimated to be 0.0422±0.0008  
4 mmol/mass of catalyst.

5 Compared to the ex-situ method for the preparation of magnetic beads, the in-situ approach  
6 was simpler and ensured a spherical and uniform shape (Fig.5) and a good rigidity of the  
7 beads with high magnetic properties. Furthermore, it exhibited, as demonstrated previously, a  
8 high catalytic activity. For these reasons, the co-precipitation method of chitosan and  
9 magnetic particles was chosen for the preparation of magnetic chitosan beads.

## 10 Figure 12

### 11 3.2.5. Comparison of the homogeneous and heterogeneous Fenton processes

12 The degradation of CDM by the electro-Fenton process was studied with the same amount of  
13 supported and free iron. The heterogeneous electro-Fenton process was found to be slightly  
14 more efficient for the removal of CDM than the homogeneous process (Fig.13). The  
15 difference was clearly more pronounced upon examination of mineralization yields,  
16 79.6±1.1% and 65.6±4.2% for the heterogeneous and homogeneous processes after 6 h of  
17 electrolysis, respectively (Table 2). This finding can be attributed to a precipitation of  
18 iron(III) in the homogeneous process which causes a reduction of the dissolved iron  
19 concentration [28]. Furthermore, homogeneous processes have some disadvantages, such as  
20 production of sludge with a high content in iron and iron deactivation by the formation of  
21 complexing agents [61].

## 22 Figure 13

### 23 3.2.6. Effect of pH

24 The solution pH is an important control parameter for maintaining the effectiveness of the EF  
25 process. Several authors [20, 27, 62-66] have reported maximum efficiency in undivided cells  
26 with carbon-felt and gas diffusion (GDE) cathodes at pH 3.0, which is close to pH 2.8 where  
27 the maximum production of •OH is expected from the Fenton's reaction. The pH was varied  
28 in the range of 2 to 7 and was found to be optimal around 3 with a total removal of CDM  
29 within 30 min. The pH was measured at the end of each test. No significant change was  
30 recorded between initial and final value of pH.



1 The low efficiency at lower pH (pH=2) could be attributed to the stabilization of H<sub>2</sub>O<sub>2</sub> which  
2 can form oxonium ion by solvating a proton. In the form of oxonium ion, hydrogen peroxide  
3 becomes electrophilic, leading to the enhancement of its stability and presumably to reduce  
4 substantial reactivity with ferrous ion as follows [67]:



6 It is remarkable from the **Figure.14** that a significant degradation of CDM occurred at neutral  
7 pH (95.6±1.7% within 60 min). However, only 32.7±2.3% of NPOC was removed after 6  
8 hours of treatment, while it was 79.7±1.7% at pH=3 (**Table.2**).

9

10

**Figure 14**

### 11 **3.2.7. Analysis of the degradation products of chlordimeform**

12 In order to elucidate a plausible reaction pathway of CDM with hydroxyl radicals generated  
13 by the heterogeneous Electro-Fenton process, a LC-MS/MS analysis was conducted to follow  
14 the gradual disappearance of the insecticide molecule as well as the formation and the  
15 disappearance of the intermediate compounds during four hours of treatment (**Figure.15**). The  
16 corresponding experiment was conducted in our optimal conditions. The identification was  
17 based on mass fragmentation values and by comparing the mass spectra to a database. The  
18 main compounds generated during the electro-Fenton treatment are described in **Table3**. The  
19 evolution of the intermediate products formed during electrolysis is shown in **Fig.16**.  
20 Degradation products of CDM were named CDM<sub>1...3</sub>.

21 The oxidation of these derivatives with the electro-Fenton process led to the formation of  
22 short chain carboxylic acids which are the last by-products before mineralization; acetic acid  
23 (tr =3.35 min), formic acid (tr =4.02 min), succinic acid (tr= 15.23 min) and oxalic acid (tr=  
24 22.14 min) were the main acids identified by ion chromatography in the final stage of CDM  
25 degradation; their retention times were compared with standard compounds. Time-courses of  
26 the carboxylic acid concentrations during treatment are given in **Fig.17**. The fluctuation of  
27 acetic acid concentration can be explained by the high affinity in water between chitosan and  
28 this acid as reported by Shamov et al [68].

29 The anions analysis by ion chromatography shows that the mineralization of CDM was  
30 accompanied by the conversion of its by-products into inorganic salts (data not shown). The  
31 CDM contains an atom of chlorine and two atoms of nitrogen. Therefore, the detection of  
32 inorganic salts such as chloride Cl<sup>-</sup> and nitrates NO<sub>3</sub><sup>-</sup> was expected. However no nitrite NO<sub>2</sub><sup>-</sup>

1 ions were produced. 25% of the expected amount of chloride ions from the target molecule  
2 was detected after 6 hours of electrolysis. Nevertheless, a negligible amount of  $\text{NO}_3^-$  was  
3 quantified during the electro-Fenton treatment. This could be explained by the nitrogen  
4 transformation into ammonium ions  $\text{NH}_4^+$ . For this reason, an assay was conducted in our  
5 optimal experimental conditions for the removal of CDM to quantify the amount of  
6 ammonium ions during treatment. The determination of the  $\text{NH}_4^+$  amount was performed by  
7 the Nessler spectrophotometric method. Results showed that after 6 hours of electrolysis, the  
8 totality of the nitrogen present in the target molecule was transformed to ammonium ions.

9 The mechanism for CDM degradation by hydroxyl radical in water has not been yet discussed  
10 in the available literature. However, Shengmin Sun et al [69], have studied this reaction in the  
11 atmosphere and they proposed several reaction channels including possible reactions initiated  
12 by hydroxyl radicals on the side chain and the benzene ring. Therefore, in Fig.18 two  
13 plausible mineralization sequences are proposed for CDM removal during the electro-Fenton  
14 process on the basis of the identified intermediates including the two possibilities of reaction  
15 of hydroxyl radicals: one on the aromatic ring (**mechanism I**) and the other on the side chain  
16 (**mechanism II**). A thorough theoretical investigation [69] demonstrated that the reaction of  
17 the carbon-nitrogen double bond is the major channel, while the abstraction reaction from the  
18 benzene ring of CDM is the least competitive method.

19 In fact, the main proposed reaction was the electrophilic addition of a hydroxyl radical on the  
20 side chain (**mechanism II**) leading to the formation of chlortoluron. In a second step the  
21 removal of chloride atom would lead to the production of a substituted urea (1,1-dimethyl-3-  
22 (2-methylphenyl)urea). The next proposed step was the elimination of the  $\text{C}_2\text{H}_6\text{N}$  molecule,  
23 which would lead to the production of a substituted alcohol ([1-  
24 methylphenyl)amino]methanol). This is the final detected by-product prior to the ring-  
25 opening and the formation of short chain carboxylic acids.

26

27

**Figure.15**

28

**Table.3**

29

**Figure 16**

30

**Figure 17**

31

**Figure 18**

32

### 1 3.2.8. Reusability of the catalyst

2 One of the most important advantages of heterogeneous catalysis is the reusability of the  
3 catalyst. To evaluate the stability of the catalytic activity of Fe<sub>3</sub>O<sub>4</sub>-Cs beads, the same catalyst  
4 was used successively four times. As can be seen, the catalyst can be reused four times  
5 without loss of its catalytic performance (Fig.19). After four times of catalyst usage, only  
6 5.4% decrease of the mineralization yield was found. From these, Fe<sub>3</sub>O<sub>4</sub>-CS beads were found  
7 to be a stable and reusable catalyst in the heterogeneous electro-Fenton process. The  
8 quantitative results of the amount of leached iron showed a zero iron concentration after 24  
9 hours of electrolysis time using the same catalyst. The negligible leaching of iron (inferior to  
10 the detection limit of the analysis technique estimated to 3.1 μmol.L<sup>-1</sup>) is due to the complex  
11 formation between amino groups of chitosan and iron as described previously. This is why the  
12 contribution of the leached iron in our heterogeneous system can be excluded and it can be  
13 affirmed that active catalytic sites are located on Fe<sub>3</sub>O<sub>4</sub>-Cs beads.

14 Furthermore, the molar ratio Fe<sup>2+</sup>/Fe<sup>3+</sup> is one of the most important operating factors that  
15 influence the characteristics of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, and it can affect the catalytic performance  
16 of our catalyst [70-72]. For this reason, the evolution of the molar ratio Fe<sup>2+</sup>/Fe<sup>3+</sup> was  
17 controlled during the preparation of Fe<sub>3</sub>O<sub>4</sub>-Cs beads and during the electrolysis assays. The  
18 experimental Fe<sup>2+</sup>/Fe<sup>3+</sup> molar ratio being of the order of 0.517±0.028, 0.481±0.001 and  
19 0.512±0.015 in CS/iron salts gel solution (before the synthesis of Fe<sub>3</sub>O<sub>4</sub>) and in wet and dry  
20 Fe<sub>3</sub>O<sub>4</sub>-Cs beads (after the synthesis of Fe<sub>3</sub>O<sub>4</sub>) samples respectively (Table 4), namely close to  
21 the theoretical ratio of 0.5, proves that the synthesized magnetite product is pure enough [73].  
22 During electrolysis, the molar ratio Fe<sup>2+</sup>/Fe<sup>3+</sup> in Fe<sub>3</sub>O<sub>4</sub>-Cs beads slightly decreased from initial  
23 value estimated to be 0.512±0.015 to 0.422±0.088 after 24 hours of electrolysis, with a  
24 negligible decrease of its catalytic performance as mentioned previously. This can be  
25 explained by the instability of magnetite under oxidizing conditions (O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>) where it is  
26 slowly oxidized to maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) which has the same spinal structure but contains only  
27 Fe(III) [72].

28 **Figure 19**

29 **Table 4**

## 30 4. Conclusion

1 Magnetic chitosan beads ( $\text{Fe}_3\text{O}_4\text{-Cs}$ ) were prepared in one step by a simple co-precipitation  
2 method.  $\text{Fe}_3\text{O}_4\text{-Cs}$  beads exhibited a catalytic performance for the degradation of CDM by an  
3 EF process with a high magnetic recovery. Our heterogeneous  $\text{Fe}_3\text{O}_4\text{-Cs-EF}$  system showed a  
4 higher performances compared to the conventional EF process using the same amount of iron.  
5 The effect of the amount of iron in chitosan beads was investigated. The optimal content was  
6 found to be  $0.104\pm 0.001$  mmol; complete CDM removal was observed within 30 min at an  
7 initial pH of 3.0, a cathodic current intensity of -5 mA and in the presence of  $0.5 \text{ g.L}^{-1}$  catalyst  
8 amount. In terms of organic carbon removal, about 80% mineralization yield was reached in  
9 the optimal conditions after 6 h of heterogeneous electro-Fenton treatment time. A kinetic  
10 analysis showed that the removal of CDM by  $\text{Fe}_3\text{O}_4\text{-Cs}$  beads followed a first-order kinetic  
11 model ( $k_{\text{app}} = 0.160 \text{ min}^{-1}$ ). The intermediate by-products including short-chain carboxylic  
12 acids were identified and their evolution during the EF treatment was followed leading to the  
13 proposal of a degradation pathway for chlordimeform via hydroxyl radicals.

14 The recyclability of the catalyst was shown since it can be reused at least four times with a  
15 good catalytic performance. The main advantage which provides the stability of our catalyst is  
16 the combination between amino groups of chitosan and iron in the structure of  $\text{Fe}_3\text{O}_4\text{-Cs}$  that  
17 minimize the possibility of iron leaching and inhibits the aggregation of  $\text{Fe}_3\text{O}_4$  nanoparticles  
18 which display a superparamagnetic property ( $\text{Fe}_3\text{O}_4$  size=10.2 nm), giving to our catalyst an  
19 additional stability limiting its loss of dispersibility in the absence of magnetic field.  
20 Furthermore,  $\text{Fe}_3\text{O}_4\text{-Cs}$  offers many advantages: low cost and toxicity, availability and  
21 environmentally friendly potential which make this catalyst a good candidate for industrial  
22 application in the field of water treatment.

## 23 **5. Acknowledgement**

24 This research was supported by Tunisian Ministry of Higher Education and Scientific  
25 Research. The corresponding author is grateful to Wafa Najjar from the National Center for  
26 Research in Materials Sciences (CNRSM, Tunisia) for the FTIR and XRD analysis.

27

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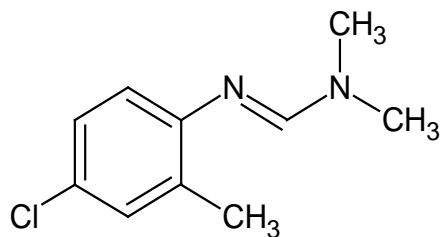
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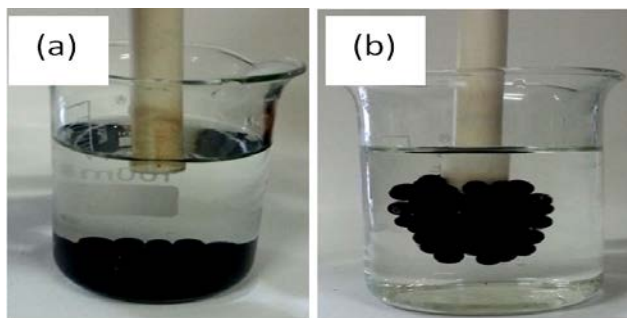
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4 **List of figures**

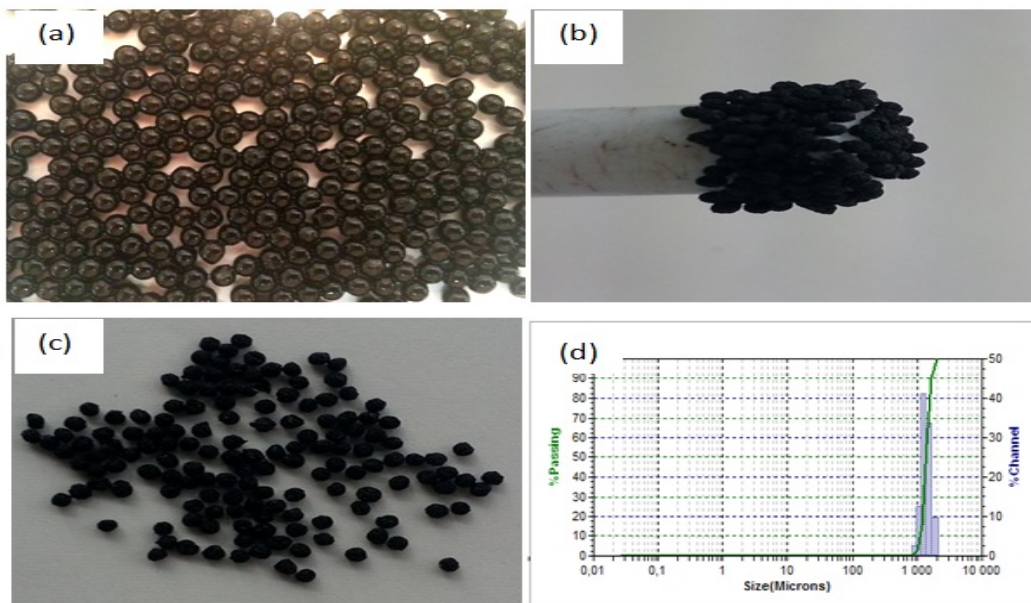
5 In print, figures should be colored.



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7 **Fig.1.** Chlordimeform molecule.  
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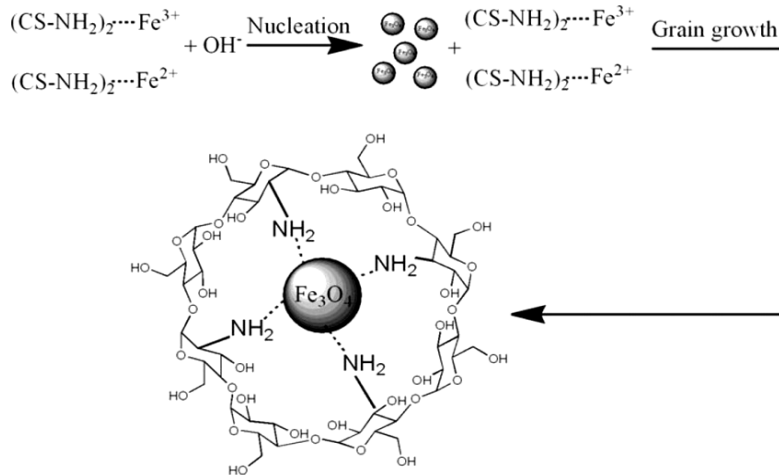


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10 **Fig.2.** Superparamagnetic behaviors of the magnetic gel beads: (a) without external magnetic  
11 field and (b) its magnetic properties when an external field was applied.  
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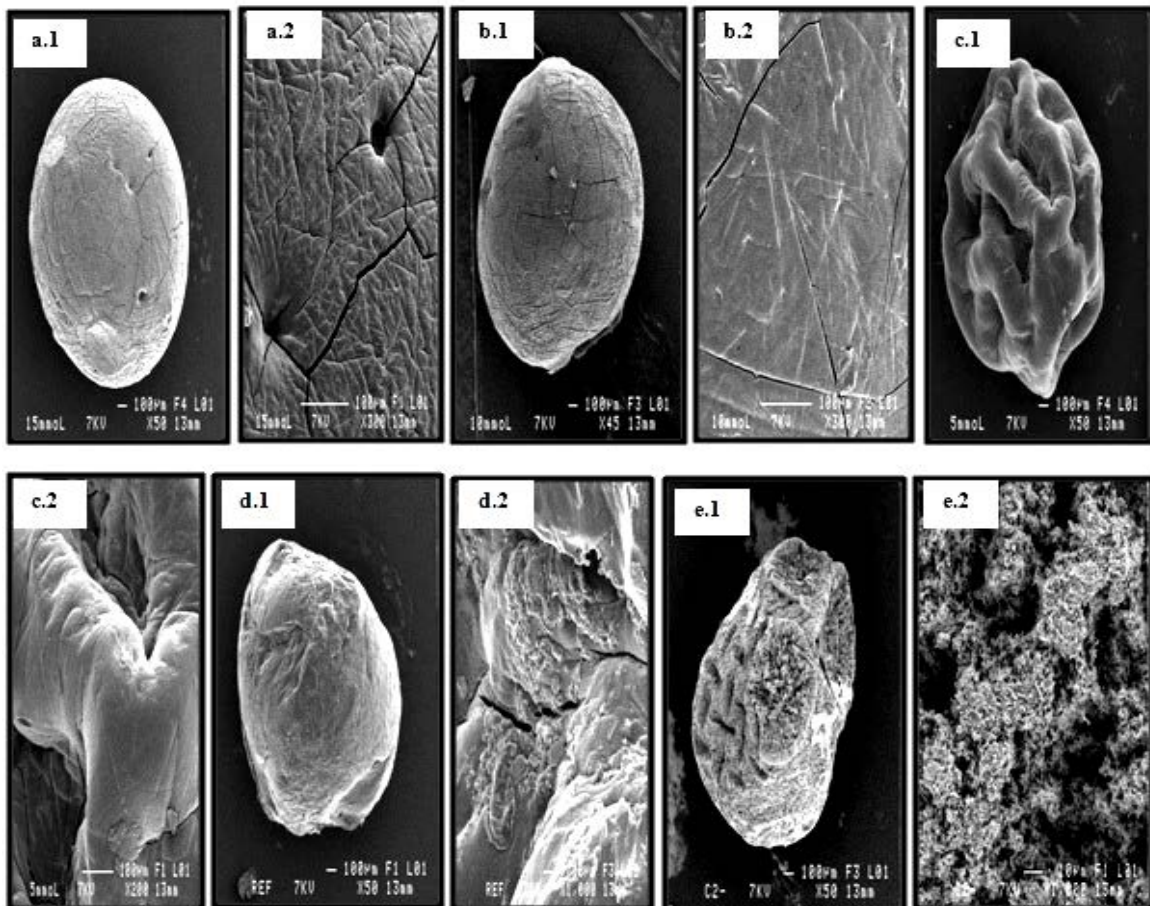


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1 **Fig.3.** Digital photographs of the magnetic chitosan beads prepared by the approach in-situ:  
 2 (a) wet beads; (b) dry beads with external magnetic field; (c) dry beads without external  
 3 magnetic field (d) **The schematic of laser diffractometry measurement for Fe<sub>3</sub>O<sub>4</sub>-Cs**  
 4 **beads.**  
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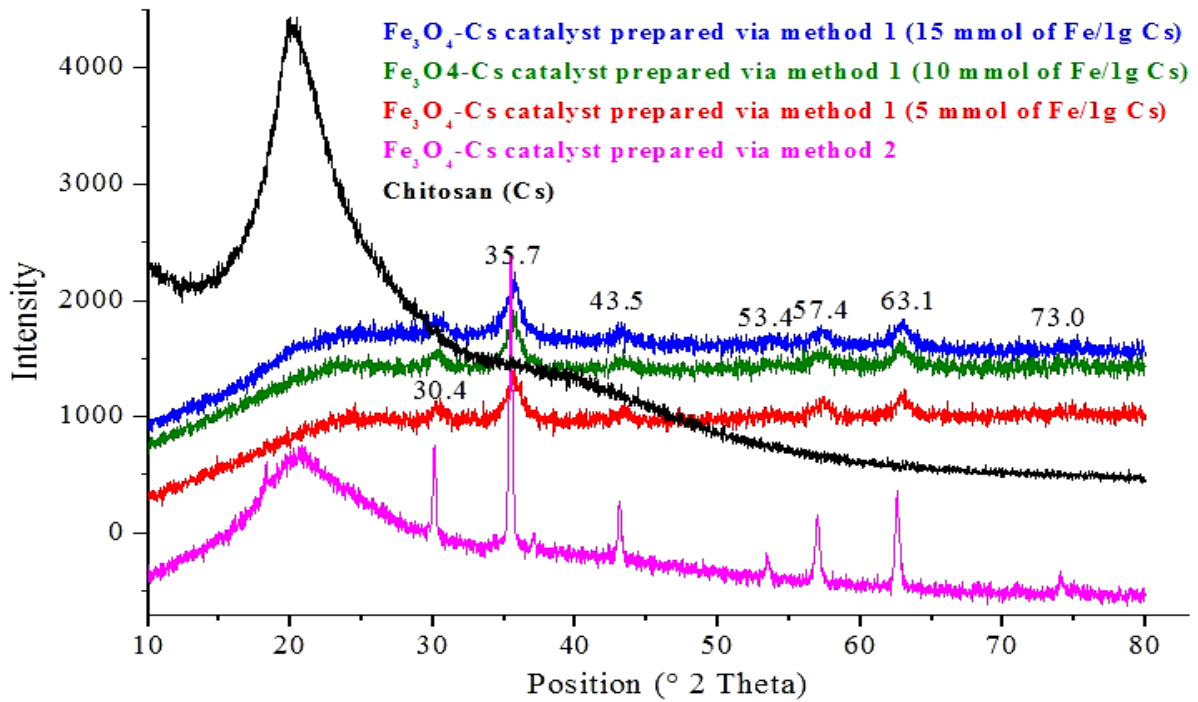
7 **Fig.4.** Principle of in-situ mineralization of magnetite nanoparticles in chitosan hydrogel [37].  
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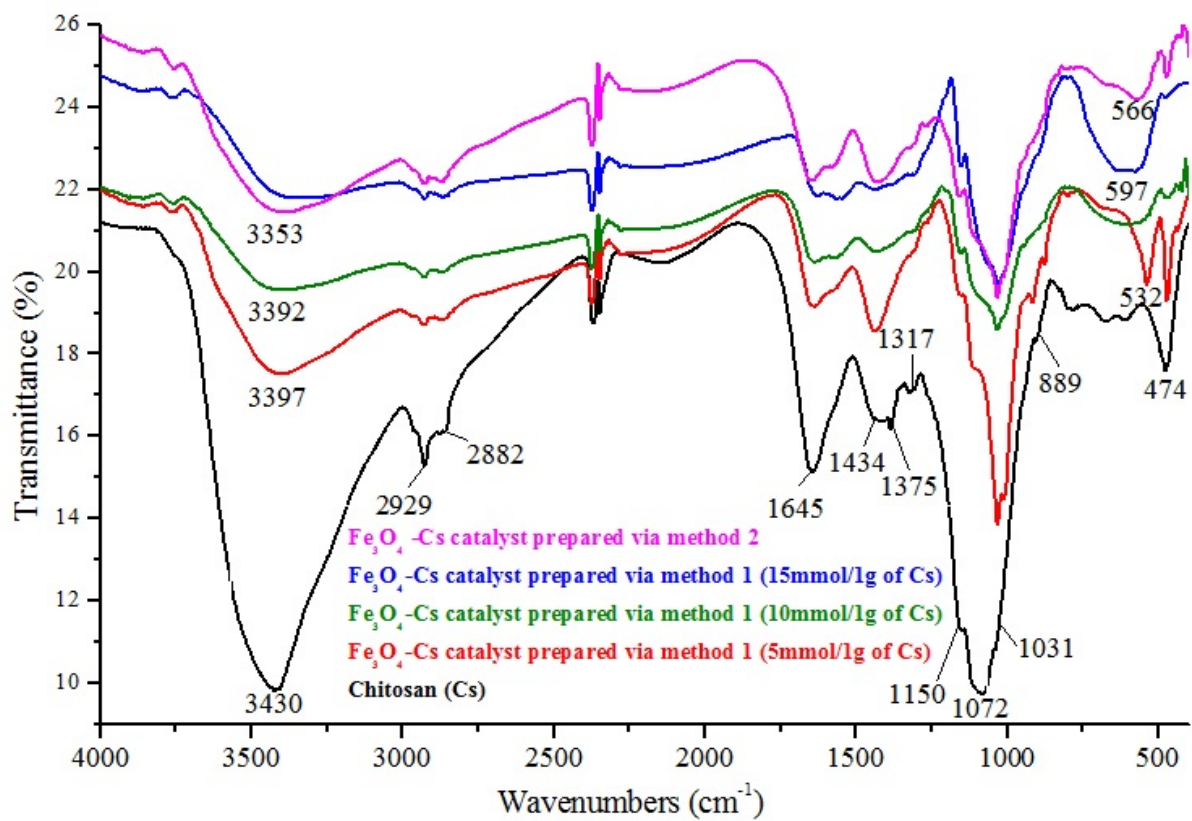
1 **Fig.5.** Morphology of catalysts: (a,b,c)  $\text{Fe}_3\text{O}_4$ -Cs beads prepared via method 1 (a) 15 mmol of  
2 Fe/ 1 g of Cs (b) 10 mmol of Fe/1 g of Cs (c) 5mmol of Fe/1 g of Cs; (d) virgin chitosan  
3 beads; (e)  $\text{Fe}_3\text{O}_4$ -Cs beads prepared via method 2.

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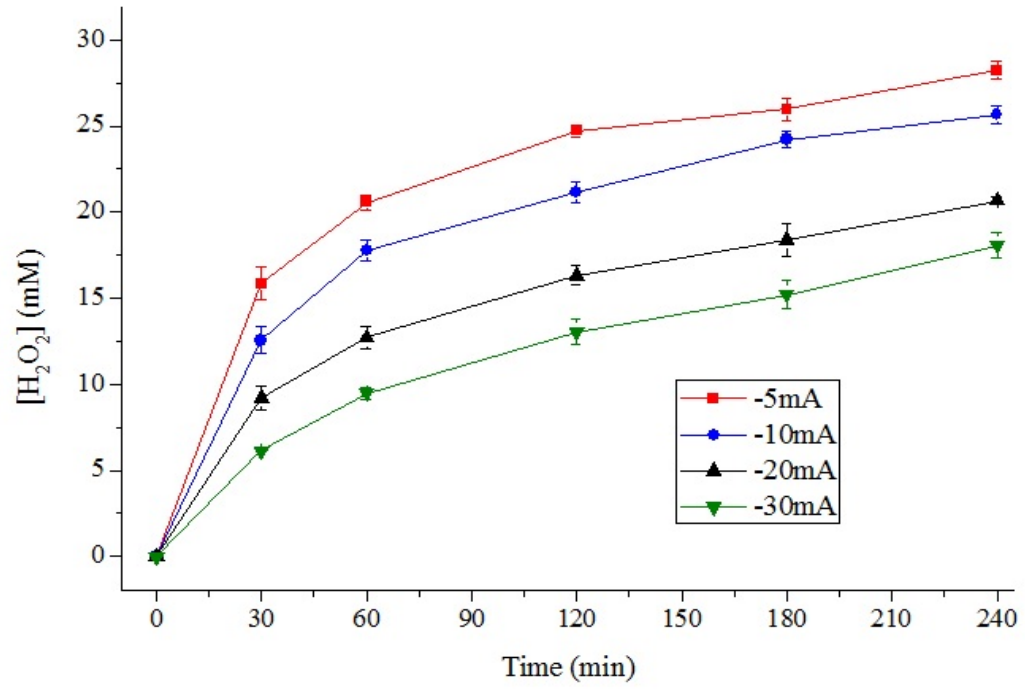
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**Fig.6.** X-ray powder diffractograms of the prepared magnetic chitosan beads.



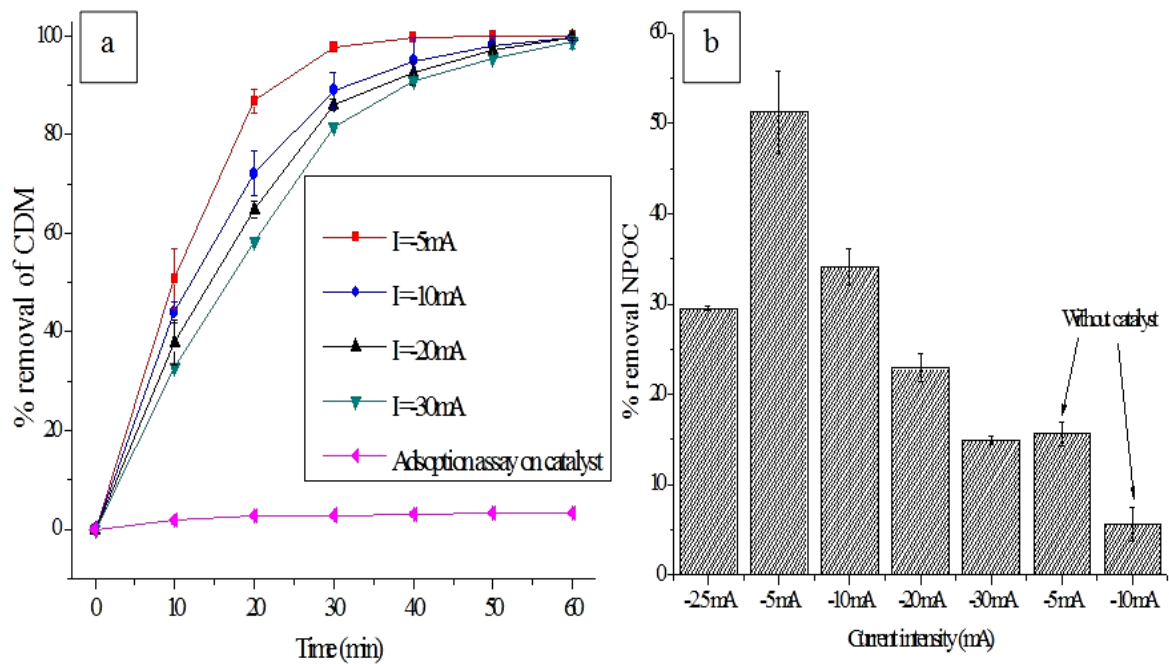
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**Fig.7.** FTIR spectra of the used catalysts.

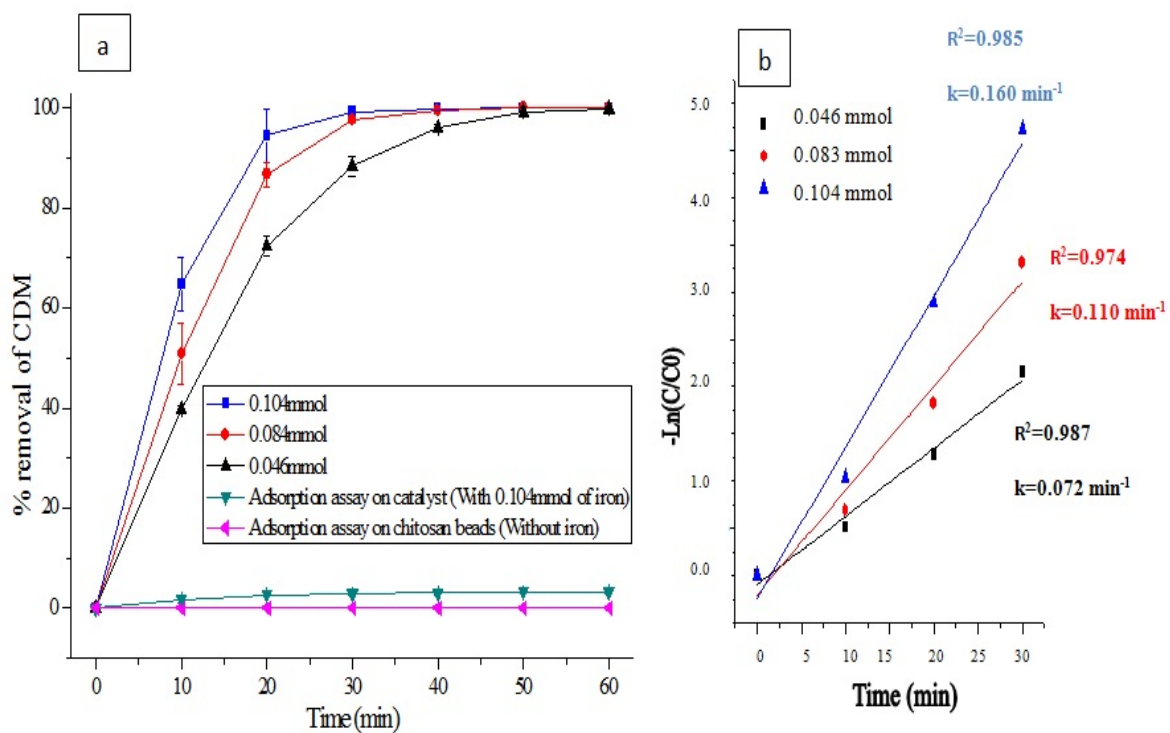


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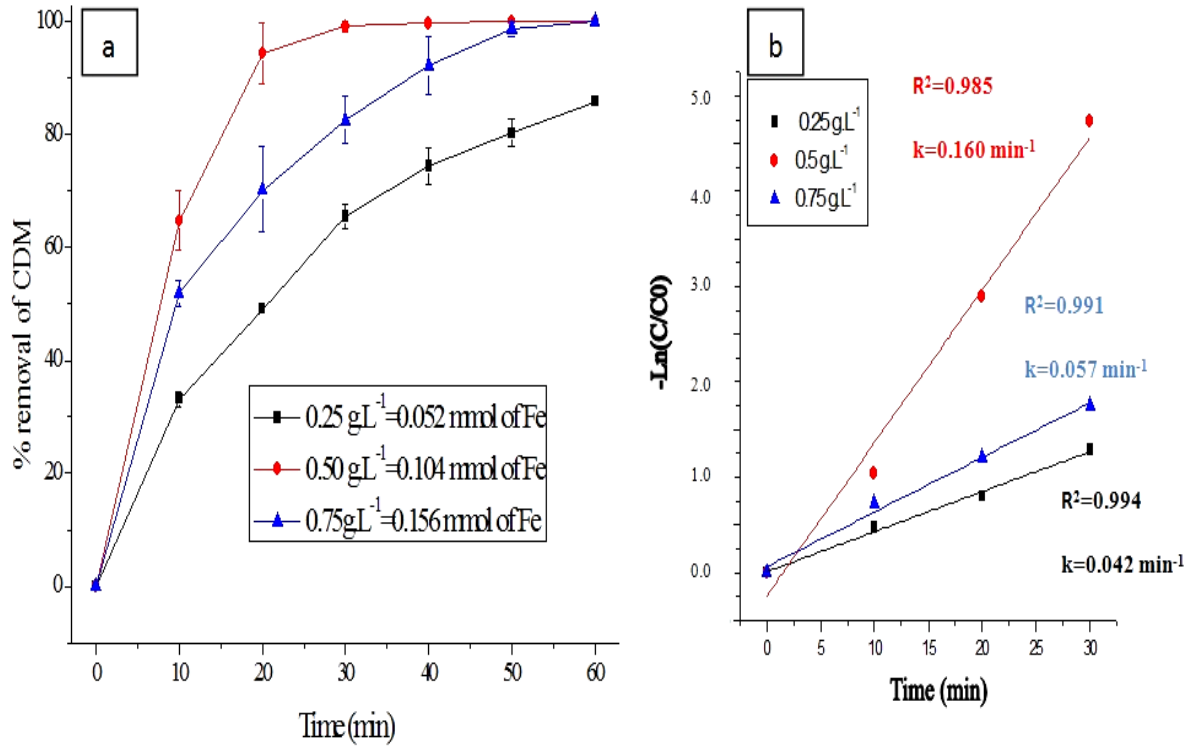
**Fig.8.** Effect of the applied cathodic current on the change of accumulated hydrogen peroxide concentration with time during electrolysis of 30 mL of a 0.05 M Na<sub>2</sub>SO<sub>4</sub> at pH=3.



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 2 **Fig.9.** Effect of the current intensity: [CDM]= 37.5 mg.L<sup>-1</sup>; pH=3; The amount of Fe/mass of  
 3 catalyst=0.083 mmol, [catalyst]=0.5 g.L<sup>-1</sup>.



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 5 **Fig.10.** Effect of the amount of iron supported in chitosan beads: [CDM]=37.5 mg.L<sup>-1</sup>; pH=3;  
 6 [catalyst]=0.5 g.L<sup>-1</sup>.

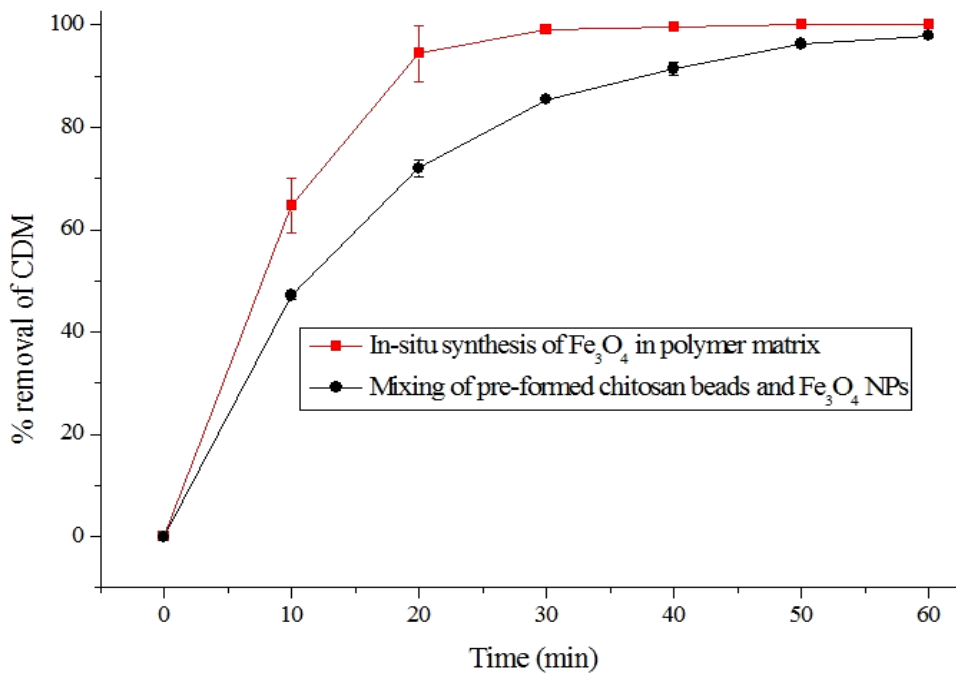


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**Figure.11.** Effect of the concentration of catalyst: [CDM]=37.5 mg.L<sup>-1</sup>; pH=3.

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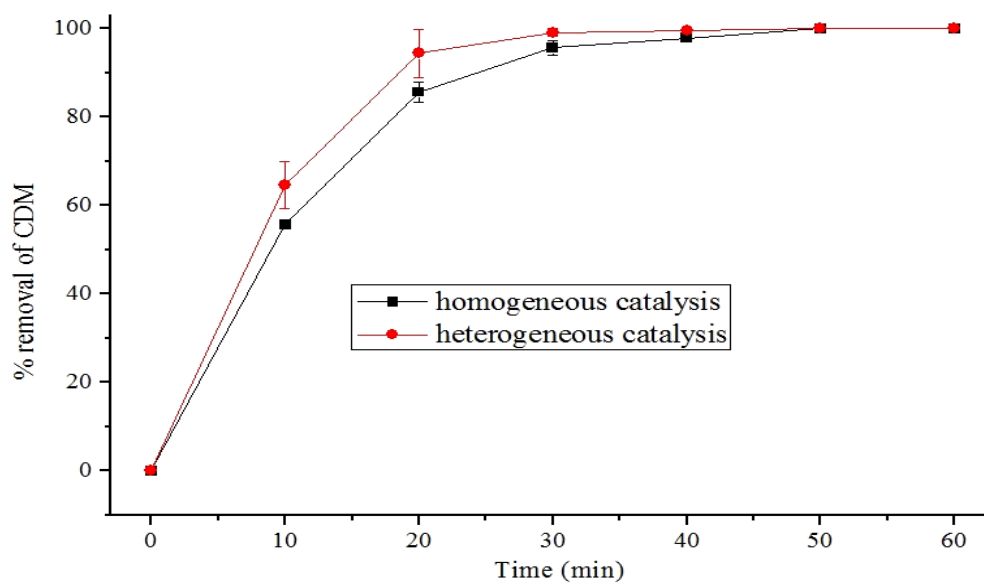
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**Fig.12.** Effect of the preparation method of catalyst: [CDM]=37.5 mg.L<sup>-1</sup>; pH=3 and [catalyst]=0.5 g.L<sup>1</sup>.

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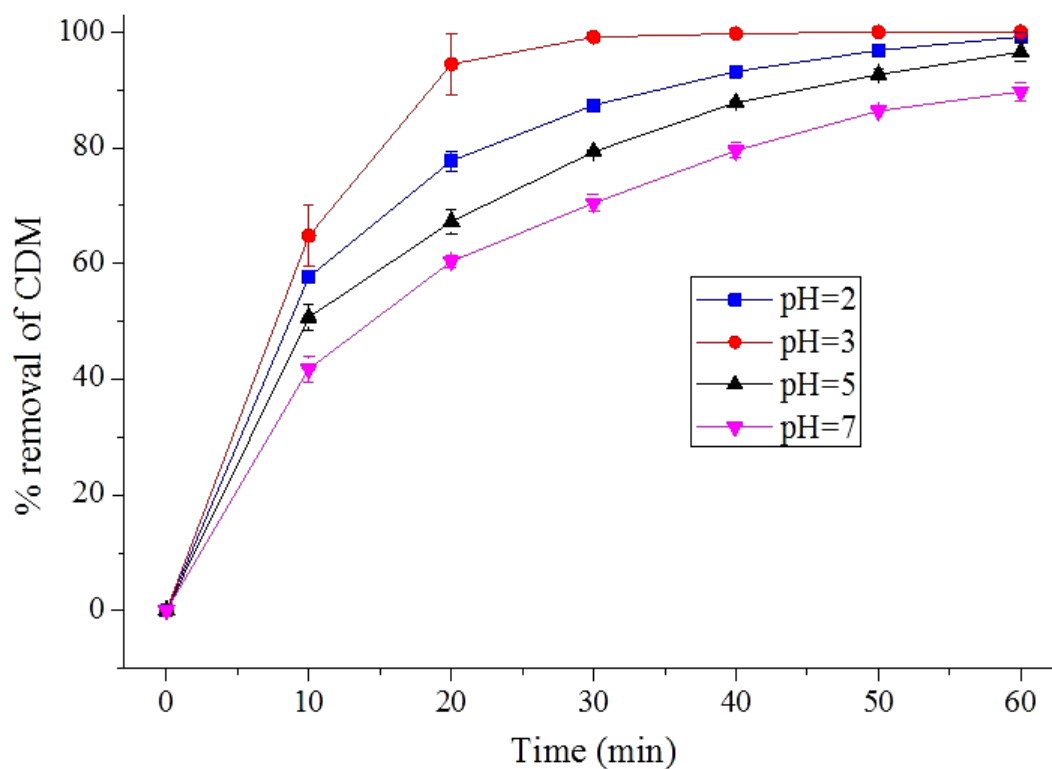
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4 **Fig.13.** Comparison of heterogeneous and homogeneous electro-Fenton processes:

5 [CDM]=37.5 mg.L<sup>-1</sup>; pH=3; [heterogeneous catalyst]=0.5g.L<sup>-1</sup>; [Fe(supported/free)]=0.1

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mmol.

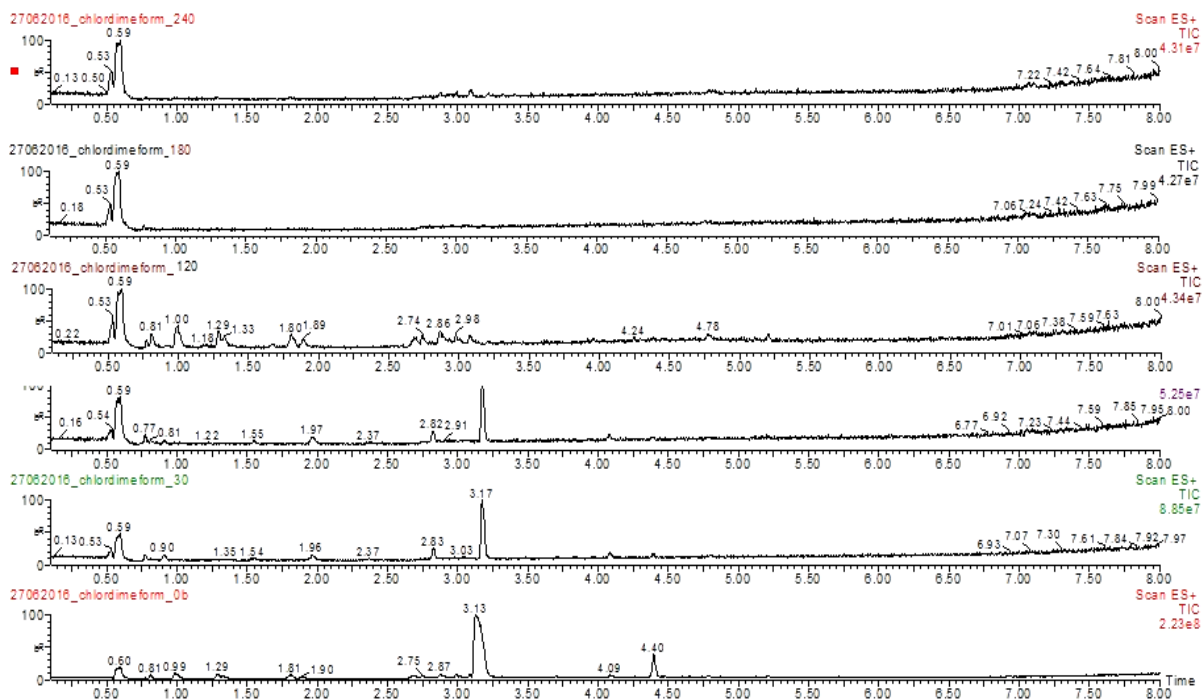


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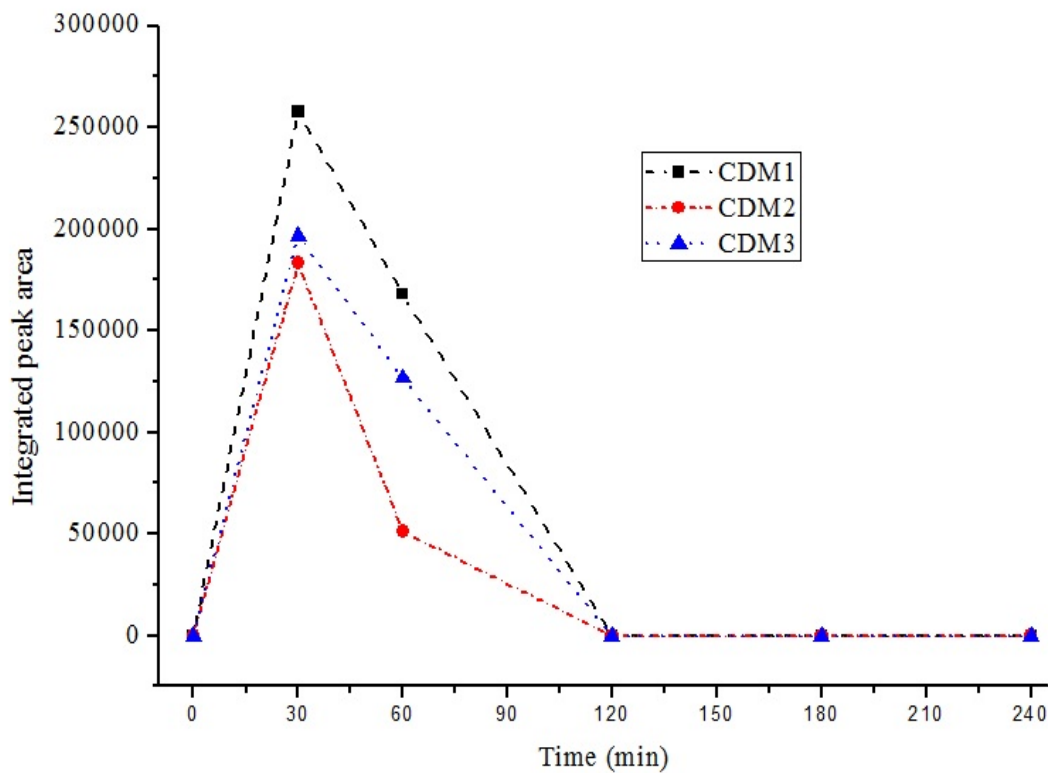
8 **Fig.14.** Effect of the pH on CDM removal by Electro Fenton process using magnetic chitosan

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beads.

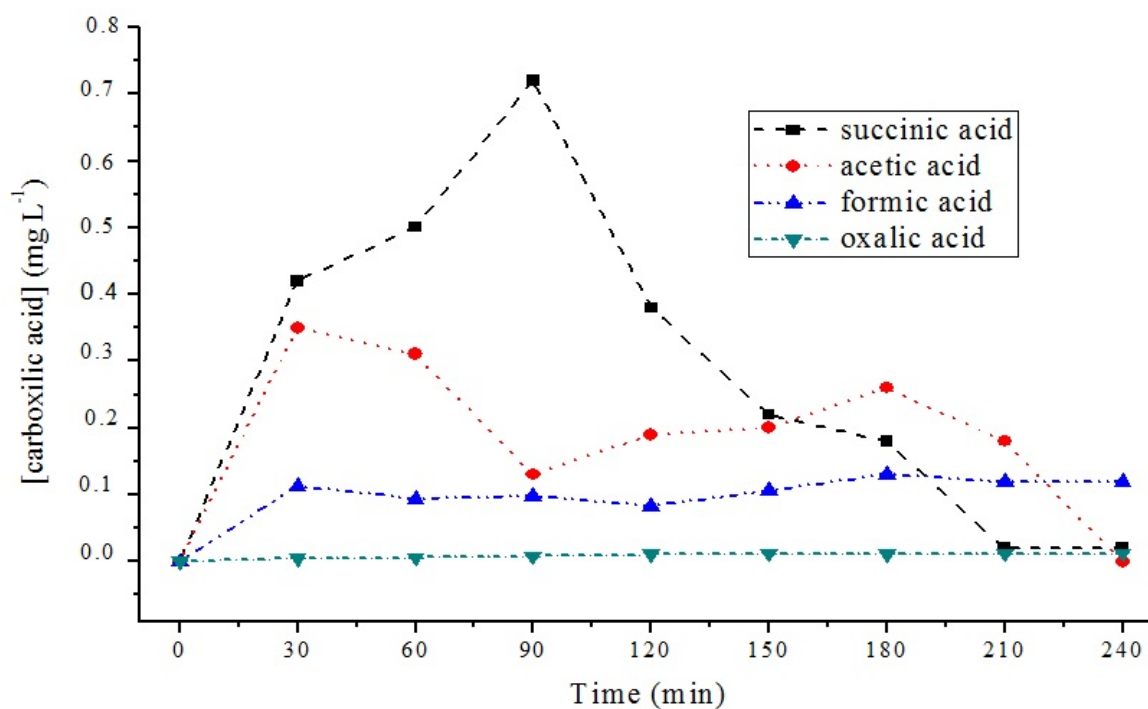


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 2 **Fig.15.** LC-MS profiles of chlordimeform obtained during an heterogeneous electro-Fenton  
 3 process with a working volume of 30 mL,  $i_{imp}=-5$  mA, pH=3 and  $[catalyst]=0.5$  g.L<sup>-1</sup>,  $n_{Fe/mass}$   
 4 of catalyst= $0.104\pm 0.001$  mmol.

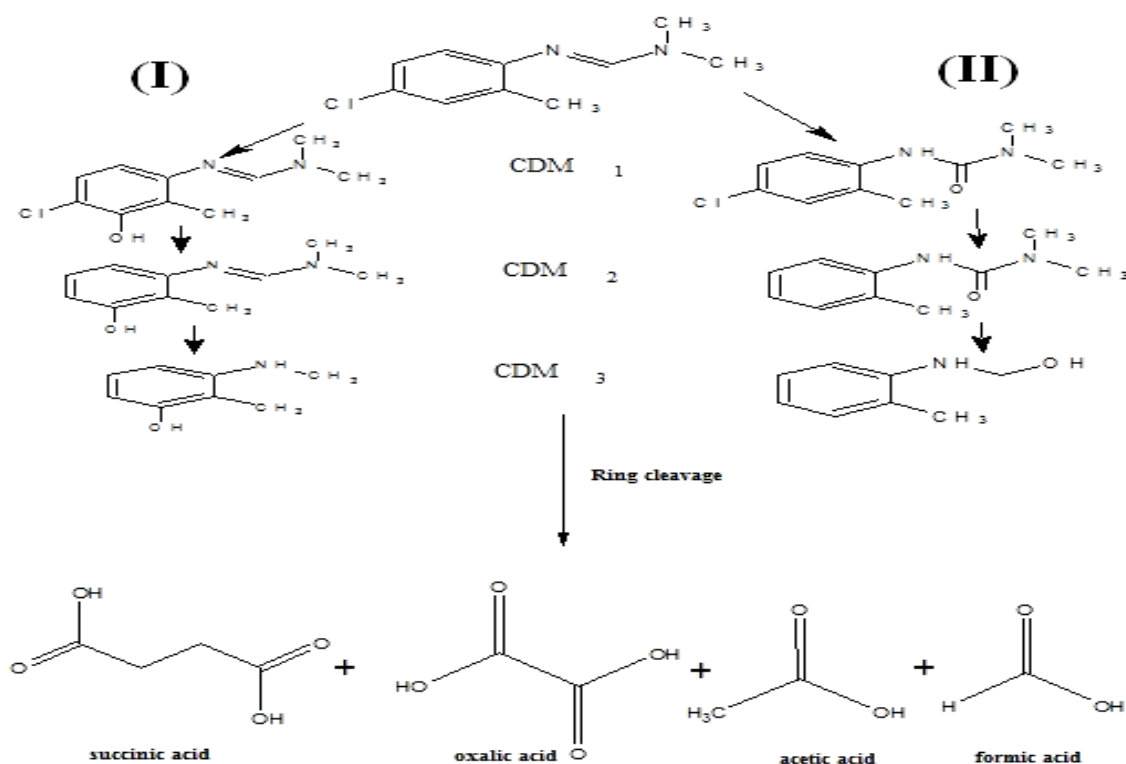


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 6 **Fig.16.** Evolution of selected intermediates during the degradation of CDM under the  
 7 conditions of Figure 15.

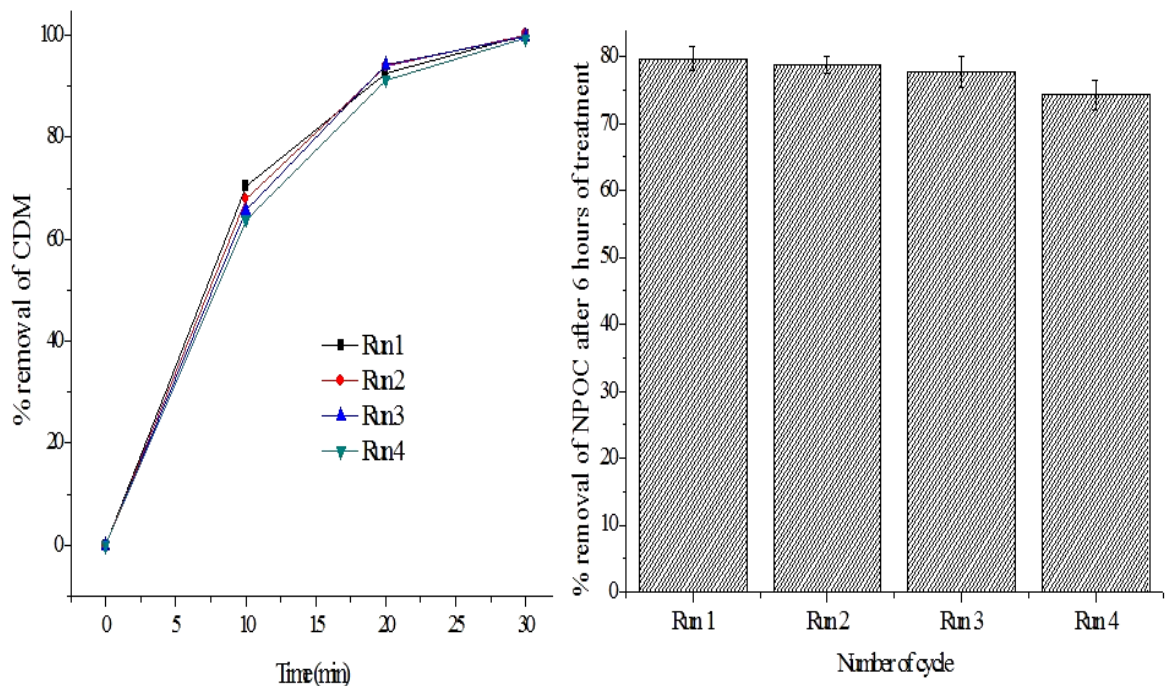




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2 **Fig.17.** Evolution of the formed carboxylic acids during the degradation of CDM under the  
3 conditions of Figure 15.



**Fig.18.** Plausible degradation pathways of chlordimeform by the heterogeneous Electro-Fenton process.



**Fig.19.** Reusability of the catalyst

#### List of Tables

**Table.1.** The amount of iron in 15 mg mass of catalyst.

Samples	<i>Fe<sub>3</sub>O<sub>4</sub>-Cs beads prepared via method 1</i>			<i>Virgin Cs</i>	<i>Fe<sub>3</sub>O<sub>4</sub>-Cs beads prepared via method 2</i>
	<i>(amount of iron/1g of Cs)</i>				
	<i>5mmol</i>	<i>10mmol</i>	<i>15mmol</i>		
<i>pH (zpc)</i>	7.2	7.1	7.2	7.2	7
<i>[Fe] (mmol/mass catalyst)</i>	0.046±0.001	0.083±0.003	0.104±0.001	0	0.0422±0.0008

**Table.2.** Summary table of mineralization rates for each experiment.

Parameter	Essay	% removal of NPOC after 6 h of treatment
The amount of iron per mass of catalyst	0.046 mmol	61.4 ± 2.1
	0.083 mmol	70.1 ± 0.7
	0.104 mmol	79.7 ± 1.7

<b>The catalyst dosage</b>	0.25 g.L <sup>-1</sup>	63.5 ± 0.8
	0.5 g.L <sup>-1</sup>	79.7 ± 1.7
	0.75 g.L <sup>-1</sup>	71.8 ± 1.3
<b>The preparation method of catalyst</b>	In-situ synthesis of Fe <sub>3</sub> O <sub>4</sub> on polymer matrix	79.7 ± 1.7
	Mixing of pre-formed C <sub>S</sub> beads and Fe <sub>3</sub> O <sub>4</sub> NPs	37.8 ± 2.3
<b>Type of EF process</b>	Heterogeneous process	79.7 ± 1.7
	Homogeneous process	65.6 ± 4.2
<b>pH</b>	pH = 3	79.7 ± 1.7
	pH = 7	32.7 ± 2.3

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9 **Table.3.** LC–MS/MS identification of the chemical formula, retention time and main mass  
10 fragmentation values of identified chlordimeform (CDM) intermediates formed during the  
11 heterogeneous Electro-Fenton process.

Compound	Formula	tr (min)	M (g.mol <sup>-1</sup> )	m/z (ES+)
CDM	C <sub>10</sub> H <sub>13</sub> ClN <sub>2</sub>	3.13	196	197
CDM 1	C <sub>10</sub> H <sub>13</sub> ClN <sub>2</sub> O	2.83	212	213
CDM 2	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub> O	0.90	178	179
CDM 3	C <sub>8</sub> H <sub>11</sub> NO	1.97	137	138

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14 **Table.4.** Evolution of the Fe<sup>2+</sup>/Fe<sup>3+</sup> molar ratio.

Sample	Molar ratio Fe <sup>2+</sup> /Fe <sup>3+</sup>
Cs/iron salts gel solution	0.517±0.028
Wet Fe <sub>3</sub> O <sub>4</sub> -Cs bead	0.481±0.001
Dry Fe <sub>3</sub> O <sub>4</sub> -Cs bead	0.512±0.015
After 6 hours of electrolysis	0.451±0.039
After 12 hours of electrolysis	0.435±0.114
After 18 hours of electrolysis	0.433±0.078

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After 24 hours of electrolysis	0.422±0.088
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