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# Raw clays from Morocco for degradation of pollutants

# by Fenton-like reaction for water treatment

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## Abstract

Three raw clays from Morocco were used as heterogeneous catalysts for Fenton-like oxidation of organic pollutants in water. The selected pollutants were two dyes used in the textile industry, Congo Red (CR) and Tartrazine (Tar, known also as a food coloring compound, E102) and Caffeine (Caf), a stimulant drug present in popular beverages such as coffee and tea, commonly used in Morocco. Two different processes were used for their degradation: (i) Fenton-like reaction; and (ii) electro-Fenton-like reaction. Process (i) was used for Tar and Caf degradation in the presence of clays from different region of Morocco (Middle Atlas - $Clay_{MA}$, Fez - $Clay_F$, and Ourika - $Clay_O$), the best results being obtained with $Clay_O$ and $Clay_{MA}$, on which 60.0 and 23.4 % of conversion and 41.0 and 20.5 % of mineralization were achieved for Tar and Caf, respectively. Process (ii) was used for degrading CR by clay-modified electrodes (CME) using the rawclays from Fez and Ourika regions ($Clay_F$ and $Clay_O$). The stability of the CME was assessed by cyclic voltammetry studies, which proved that they are stable in the experimental conditions used. The electrodegradation of CR dye, performed without hydrogen peroxide in the reaction medium, achieve 67.0 % of mineralization at the end of electrolysis (2 h).

## 1. Introduction

The 2030 Agenda for Sustainable Development with its 17 sustainable development goals (SDGs) from the United Nations (UN) aims to end poverty, conserve biodiversity, combat climate change and improve the livelihoods of people everywhere (Axon and James, 2018; United Nations, 2016). In the 17 SDGs, water and the use of raw materials are interlinked, and chemistry and geochemistry are two of the keys to achieve these goals in order to preserve society and the planet for the future generations (Anastas and Zimmerman, 2016; United Nations, 2023). Moroccan raw clays were utilized as

heterogeneous catalysts to eliminate pollutants from effluents in order to tackle the issue of clean water through the valorization of raw materials via the oxidation Fenton reaction. Morocco is a country with important deposits of clays and these geological materials are very attractive to apply as adsorbents (Bencheqroun et al., 2019a) or heterogeneous catalysts for Fenton-like oxidation (Assila et al., 2023a).

Porous materials as clays offer a word of possibilities for preparing heterogeneous catalysts due to their stability in different pH ranges, easily separation, and reutilization. Several examples were find in literature using the clays as heterogeneous catalysts (Aid et al., 2017; Hadjltaief et al., 2019; Herney-Ramirez et al., 2010). The degradation of reactive blue 19 was performed by TiO2-coated Tunisian clay synthesized by impregnation method, and the high photodegradation of dye by $TiO_2$–clay is due to the anatase phase stability of the photocatalyst (Hadjltaief et al., 2019). Montmorillonite clay combined with bentonite, acid-washed clay (K10), and Al-pillared clay underwent ion exchange with nickel for the purpose of ethylene oligomerization in a fixed-bed flow reactor, demonstrating good activity and stability (Aid et al., 2017). In the work of Jesus et al. (2022), a natural clay was using as a support for magnetite and copper-containing magnetite for heterogeneous Fenton/photo-Fenton degradation of antibiotics in wastewater treatment plants effluent.

Clays are a group of minerals used as raw materials in the ceramic, paper, and metal industries, in the field of pets feeding, and as adsorbents, discoloration agents, ion exchanger and supports (Aid et al., 2017; Antonielli et al., 2020; Hacıosmanoglu et al., 2022; Maryan et al., 2015). These minerals are phyllosilicates with basic building blocks of $Si(O, OH)_4$ tetrahedra and $M(O, OH)_6$ octahedra, and mostly $M = Al^{3+}$, $Mg^{2+}$ or $Fe^{2+,3+}$ (Assila et al., 2023a; Bencheqroun et al., 2019a; Schoonheydt, 1991).

Fenton-like oxidation reaction is very attractive, non-toxic nature, ease to use, and low cost (Fida et al., 2017; Fu et al., 2022; Liu et al., 2021, Usman et al., 2023; Wang and Tang, 2021). However, there are few examples using clays as modified electrodes for degradation of pollutants by electro Fenton-like oxidation. Electrochemistry is one of the sustainable methods to be used for the treatment of waste effluents; indeed, it does not require high temperatures, allows the achievement of high degrees of mineralization of the pollutants, and has low operational costs (Brillas et al., 2009; Chaplin, 2014). A further advantage comes from the possibility of carrying out the electrochemical process using electrodes modified with heterogeneous catalysts, due to their peculiar properties (Poza-Nogueiras et al., 2018).

The works of Ozcan *et al*. (2017) showed that iron in the kaolin clay is capable to degrade the emerging pollutant enoxacin with a TOC of 98 % after 7 h of reaction. Methylene blue was also degraded with the clay modified electrode with a chemical oxygen demand (COD) of 96.5% after 45 min of reaction (Ma et al., 2009). Modified electrodes using iron oxide supported on nanostructured allophane clays, with both $Fe^{3+}$ and $Fe^{2+}$ species on the surface, were used for degrading atrazine with higher efficiency compared to the heterogeneous Fenton-like catalysis (Garrido-Ramírez et al., 2013). The clay modified electrodes (CME) combine the advantages of the catalytic properties of the clay structures with the versatility, energy efficiency, cost effectiveness, and facility for process automation of the electrochemical processes (Herney-Ramirez et al., 2010).

Herein we report the degradation of different pollutants by Fenton-like reaction and electro Fenton-like oxidation using several raw clay minerals from Morocco. The places where the clays come from cover an important part of Morocco territory (Fig. 1), which confirms the presence of huge deposits of clay minerals in this country.

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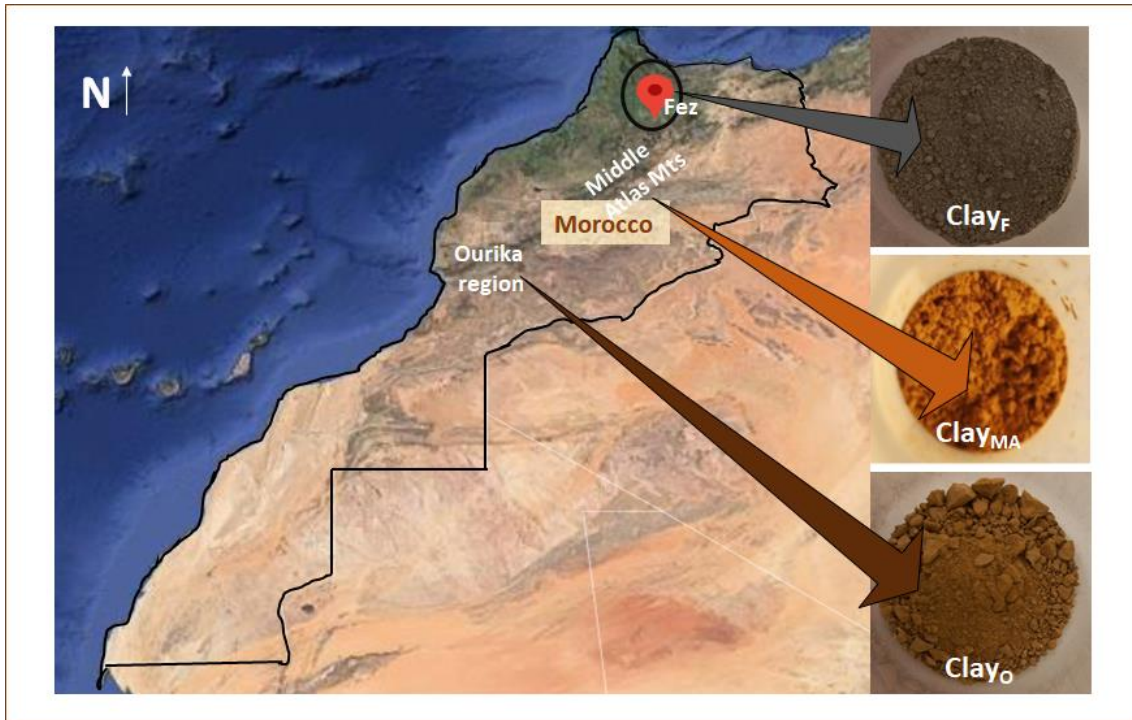
**Fig. 1.** Map of Morocco showing the location of the clays sites.

100

Two clays were collected from the Ourika region ($Clay_O$) and the city of Fez ($Clay_F$), while one sample was collected from the Middle Atlas region ($Clay_{MA}$). They were used for studying the degradation of three different organic pollutants in water. Tartrazine (Tar) and caffeine (Caf) were removed by Fenton-like reaction using the three raw clays, whereas Congo Red (CR) was degraded by electro Fenton-like oxidation using CME based on $Clay_O$ and $Clay_F$.

## 2. Experimental section

### 2.1. Preparation and characterization of the heterogeneous clay catalysts

Three raw clays from Morocco obtained from deposits located in the Middle Atlas region ($Clay_{MA}$, where MA stands for Middle Atlas), the city of Fez ($Clay_F$, where F stands for Fez), and the Ourika region ($Clay_O$, where O stands for Ourika) were used in this study without any prior activation. Samples were ground, sieved to obtain particle sizes (60 -

113    100 µm), and washed with distilled water. After that, all clays were dried at 60 ºC for 24 h

114    and stored in hermetic plastic bottles until further use.

115    In order to study the effect of the presence of the metal in the clay, heterogeneous clay

116    catalysts were prepared by addition of zinc or copper using an adapted method described

117    in (Assila et al., 2023). Typically, aqueous solutions (250 mL) containing $2.70 \times 10^{-2}$ mmol

118    of Cu or Zn were mixed with 4 g of the pristine support ($Clay_{MA}$) at pH 4.0. The

119    suspensions were stirred during 24 h at room temperature. After each ion-exchange step,

120    the suspensions were filtered-off, washed with deionized water and dried at 60 ºC

121    overnight. Finally, the solids were calcined at 350 °C during 4 h under a dry-air stream.

122    The samples were identified as $Cu$-$Clay_{MA}$ and $Zn$-$Clay_{MA}$. All clay samples were used

123    as heterogeneous catalysts for the degradation of tartrazine (Tar, $C_{16}H_9N_4Na_3O_9S_2 \geq 90\%$,

124    Sigma-Aldrich) and caffeine (Caf, $C_8H_{10}N_4O_2 \geq 99\%$, Sigma-Aldrich) in Fenton-like

125    reaction. In addition, $Clay_F$ and $Clay_O$ were used for preparing clay modified electrodes

126    (CME) for the degradation of Congo Red (CR, $C_{32}H_{22}N_6Na_2O_6S_2$, 3,3′-([1,1′-biphenyl]-

127    4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid, Sigma-Aldrich) by electro Fenton-like

128    oxidation.

129    The heterogeneous clay catalysts were characterized by different techniques, such as

130    powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), $N_2$

131    adsorption, scanning electron microscopy coupled with energy dispersive X-ray analysis

132    (SEM/EDX), and chemical analysis.

133    Mineralogical identification was performed by XRD through a Philips X'pert Pro-MPD

134    diffractometer (Philips PW 1710, APD), provided with an automatic divergence slit and

135    a graphite monochromator, using CuKα radiation powdered at 40 kV and 40 mA ($Cuk_{α1}$

136    = 1.54060 Å and $Cuk_{α2}$ = 1.54443 Å). The XRD patterns were obtained from powders

137    (bulk sample) and from oriented aggregates (< 2 µm), in the range of 2θ from 3 to 65°

138    and 3 to 35°, respectively, with a step size of 0.02° and a counting time of 1.25 s. Sample

139    preparation for XRD analysis involved gentle grinding of the solid into a fine powder and

140    packing of approximately 1.0 g of the sample into the sample holder. Identification of

141    clay minerals was obtained in the oriented aggregates after chemical and thermal

142    treatments (ethylene glycol saturation and heating at 490 °C).

143    XPS analysis was performed by recording the high-resolution and survey spectra with a

144    Kratos Axis-Supra instrument. Monochromatic X-ray source Al Kα (1486.6 eV) was used

145    for all samples and experiments. The residual vacuum in the X-ray analysis chamber was

146    maintained at around $7.2x10^{-9}$ torr. The samples were fixed to the sample holder with

147    double sided carbon tape. Due to the non-conducting nature of the samples, it was

148    necessary to use a co-axial electron neutralizer to minimize surface charging, which

149    performed the neutralization by itself. Charge referencing was done by setting the binding

150    energy of C1s photo peak at 285.0 eV C 1s hydrocarbon peak. Photoelectrons were

151    collected from a take-off angle of 90º relative to the sample surface. The measurement

152    was done in a Constant Analyser Energy mode (CAE) with a 10 mA of emission current

153    and 160 eV pass energy for survey spectra and 20 eV pass energy for high resolution

154    spectra. A wide scan survey spectrum was used to identify and quantify the elements in

155    the sample. High-resolution narrow scans are used to build the chemical state assessment,

156    as well as to quantify the presence of the reference elements in each sample. Data analysis

157    and atomic quantification were determined from the XPS peak areas using the ESCApe

158    software supplied by the manufacturer Kratos Analytical.

159    Nitrogen ($N_2$) adsorption-desorption isotherms were measured at -196 °C on ASAP2040

160    Micrometrics device endowed with a thermal conductivity detector. The prepared

161    samples were previously degassed at 90 °C for 1 h and then at 250 °C with a heating rate

162    of 5 °C $min^{-1}$ for 6 h, up to a residual pressure smaller than 0.5 Pa. The specific surface

area and pore size distribution (PSD) were determined by the Brunauer-Emmett-Teller (BET) method and Barret-Joyner-Halenda (BJH) analysis, respectively, using the adsorption branch.

SEM/EDX analysis was performed on a Phenom ProX with EDS detector (Phenom-World BV, Netherlands). All data were acquired using the ProSuite software integrated with Phenom Element Identification software, allowing the quantification of the concentration of the elements present in the samples, expressed in either weight or atomic percentages. The samples were added to aluminum pin stubs with electrically conductive carbon adhesive tape (PELCO Tabs™) and were imaged without coating. The aluminum pin stub was then placed inside a Phenom Charge Reduction Sample Holder (CHR), and different points were analyzed for elemental composition. EDS analysis was conducted at 15 kV with intensity map.

Chemical analysis was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES) for the quantification of metals in the liquid phase during the ion-exchange process using an Optima 8000 spectrometer (PerkinElmer). A 5110 ICP-OES spectrometer (Agilent Technologies) was instead used to quantify the metals in the solid samples.

**2.2 Fenton-like oxidation**

For the degradation of Tar or Caf with the different heterogeneous clay catalysts, the concentration of pollutant (30 ppm), temperature (40 ºC), and pH (=3.0) were fixed at the best values found in a preliminary study in a stirred semi-batch reactor at atmospheric pressure using Clay$_{MA}$ as catalyst (Assila et al., 2023a). Prior to experiments, all catalysts were pretreated at 100 °C for 2 h in an oven. The semi-batch reactor was loaded with 250 mL of a solution of pollutant prepared with ultrapure water produced with an ultrapure

water system (Milli-Q, EQ 7000), using 200 mg of catalyst and 5 mL of $H_2O_2$ (12 mM).

The reaction was then performed under stirring at 300 rpm, during 300 min. Sampling

was carried out at fixed time intervals and the reaction was stopped with the addition of

an excess of sodium sulphite ($Na_2SO_3$, Sigma-Aldrich), which instantaneously consumes

the unreacted $H_2O_2$. Catalytic tests were performed in duplicate, and the maximum

deviation observed in the removal of the organic pollutants was 2%. The stability of the

best clay, $Clay_O$, for Tar degradation was studied using the experimental catalytic

conditions determined above. Two cycles were performed and for each cycle, the used

catalyst was filtered-off, washed with ethanol, and dried in an oven at 70 °C overnight

before reutilization. The solution recovered after each catalytic test was analyzed by ICP-

OES to quantify the amount of the metal species eventually leached during reaction.


**2.3 Electro Fenton-like oxidation**

Clays modified electrodes (CME) were prepared using $Clay_F$ and $Clay_O$ by the procedure

already described in previous papers (Assila et al., 2023a; Ferreira et al., 2018). Typically,

CME were prepared by dispersing 20 mg of the clays powders in a mixture of 180 μL

ultrapure water (Barnsted E-pure system, 18.2 MΩ cm at 20 °C) and 180 μL Nafion®

suspension (5 wt. %, Sigma-Aldrich). The resulting suspensions were homogenized using

an ultrasound bath and totally deposited onto the wet proofed Carbon Toray paper (CT,

geometrical area of 4.0 cm$^2$, Quintech); the solvent was then evaporated at room

temperature overnight. CT paper was glued to the platinum wire using a conductive

carbon cement (Quintech) and subsequently dried at room temperature during 24 h.

A three-electrodes cell assembly composed of the reference electrode, consisting of a

saturated calomel electrode (SCE) Hg/Hg$_2$Cl$_2$ (KCl sat.) separated from the solution by a

Habber-Luggin capillary tip, a platinum foil (99, 95%) as a counter electrode, and a CME

working electrode, was used for electrochemical measurements. The electrochemical

instrumentation consisted of a potentiostat/galvanostat from Amel Instruments coupled

to a microcomputer (Pentium II/ 500 MHz) through an AD/DA converter. The Labview

software (National Instruments) and a PCI-MIO-16E-4 I/O module were used for

generating and applying the potential program as well as for acquiring data, such as

current intensities.

Prior to electrochemical measurements, the solution was de-aerated with ultra-pure $N_2$ (U

Quality from Air Liquide) for 30 min, and a nitrogen stream was maintained over the

solution during the measurements in order to avoid any dissolved oxygen interferences.

The electrocatalytic activity of CME was investigated by using cyclic voltammetry (CV)

both in the absence and in the presence of the CR dye. In the CVs, the currents were

normalized with the geometrical surface area of the working electrode to provide more

useful correlations in terms of kinetic issues. Electrolysis at a constant potential (2 V) in

the presence of dye was carried out in the same electrolytic cell used for the CV studies.

The used concentration of the CR dye was $3.44 \times 10^{-3}$ mmol (25 ppm) for CV studies and

$6.88 \times 10^{-3}$ mmol (50 ppm) for electrolysis in 0.10 M NaCl solution, at room temperature

without addition of hydrogen peroxide.


**2.5 Product analysis**

In order to quantify the extent of degradation of the organic pollutants by Fenton-like

reaction, after separation of the solid catalyst by centrifugation, an UV-vis

spectrophotometer (UV-2501PC from Shimadzu) was used at the characteristic

wavelengths $\lambda_{max}$ = 427 nm and 272 nm for Tar and Caf, respectively, in order to

determine the residual concentration of the pollutant in the reaction solution.

237 Liquid phase samples from electro Fenton-like reaction were analyzed by high

238 performance liquid chromatography (HPLC), equipped with an isocratic pump (Jasco

239 PU-980 Inteligent HPLC Pump) and a double on-line detection including an UV-vis

240 detector (Jasco Inteligent UV/vis detector). Separation of the different components was

241 carried out using the following HPLC ion exchange columns: IonPac AS11-HC from

242 Analytical, Aminex HPX-87 H ($\lambda$=210 and 260 nm) from Biorad, and RP18 from Merck

243 ($\lambda$=497 nm).

244 The total organic carbon (TOC) was determined using the NPOC method, with a

245 Shimadzu's Total Organic Carbon Analyzer TOC-L coupled with the ASI-L autosampler

246 of the same brand.

247

248 **3. Results and Discussion**

249 **3.1 Characterization of the heterogeneous clay catalysts**

250 Scanning electron microscopy (SEM) investigated the morphology of the raw clays, and

251 the textural properties were evaluated by $N_2$ adsorption analysis (Fig. 2). SEM images

252 obtained with different magnifications, show that the clays have a heterogeneous

253 morphology, with the presence of aggregates composed by particles of different size, with

254 $Clay_{MA}$ having the smallest particles. Flat intercalated layers typical of the clay minerals

255 make some of these aggregates, especially in the case of $Clay_O$. From EDX spectra, the

256 amount of the typical elements of the clays are identified, Al, Si, Na, Mg, Fe, K, Mg, Ti

257 and Ca (Table S1). The presence of iron (Fe) with 7.46 wt% for $Clay_O$, 4.38 wt% for

258 $Clay_F$ and 5.50 wt% for $Clay_{MA}$, makes these materials attractive for the Fenton reaction.

259 Furthermore, among the three types of clay, $Clay_F$ possesses the highest calcium content

260 at 8.46 wt%, followed by $Clay_{MA}$ with 2.40 wt%.

261    All clays exhibit an isotherm type IIb, according to the IUPAC (International Union of

262    Pure and Applied Chemistry) classification, with a hysteresis loop at high *P/P⁰* values,

263    typical for mesoporosity originating from interparticles voids (Bergaya, 1995; Kloprogge,

264    2998; Weidler, 1997). Fig. 2B displays the $N_2$-physisorption isotherms and the pore size

265    distribution curves of Clay$_F$ and Clay$_O$, whereas those of Clay$_{MA}$ were already reported

266    in a previous paper [Assila et al., 2023a]. The textural properties of all the pristine clays

267    are summarized in Table 1.

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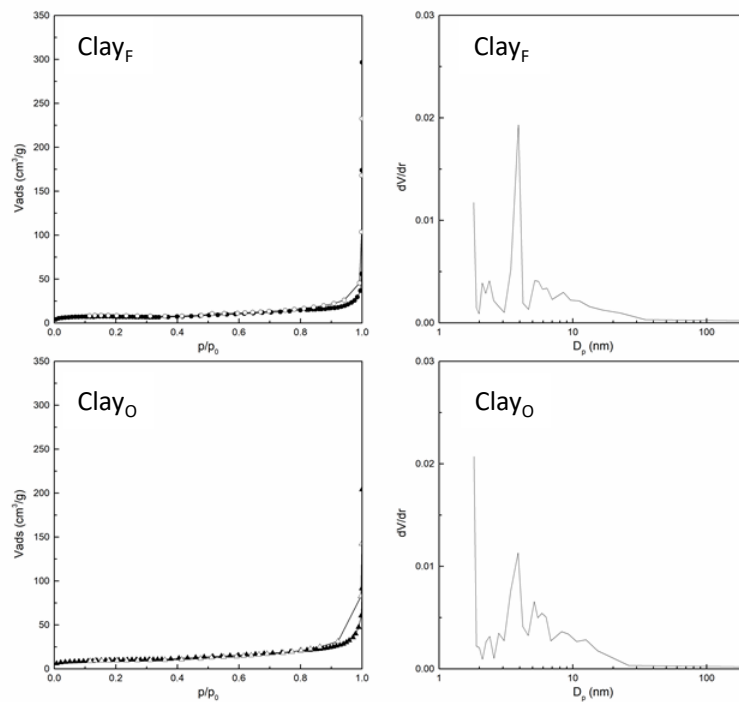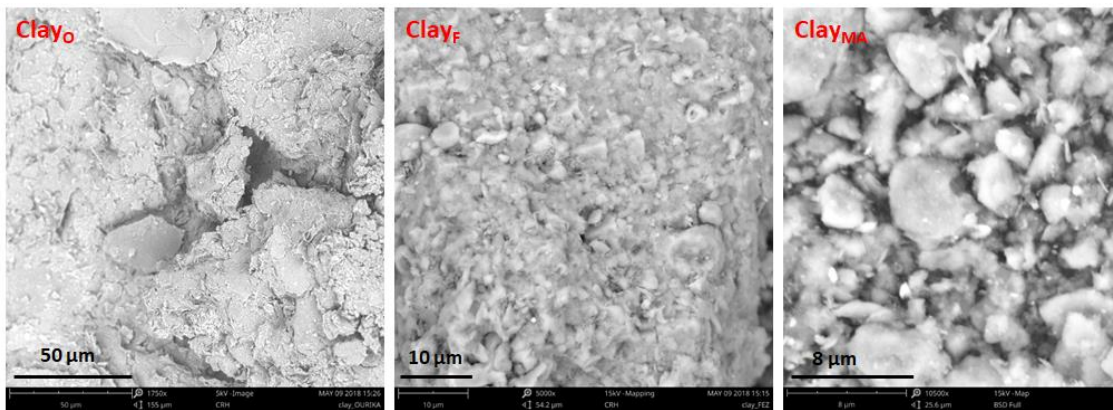
269 **Fig. 2.** A) SEM images and EDX spectra, and B) $N_2$ adsorption/desorption isotherms of

270 the pristine clays.

271

272 The specific surface areas calculated by the BET method are 22.5, 23.0, and 34.4 $m^2/g$

273 for $Clay_F$, $Clay_{MA}$ (Assila et al., 2023a), and $Clay_O$, respectively. $Clay_O$ exhibits the

274 highest values of both $S_{BET}$ and $V_{total}$ (1.5 times greater than those of $Clay_F$). On the other

275 hand, although they have similar surface areas, $Clay_{MA}$ has a significantly lower pore

276 volume than $Clay_F$.

277

278 **Table 1.** Textural properties of the pristine clays.

279

| Samples | $S_{BET}{}^a$ ($m^2/g$) | $V_{total}{}^b$ ($cm^3/g$) |
|---|---|---|
| $Clay_F$ | 22.5 | 0.060 |
| $Clay_{MA}$ (Assila et al., 2023a) | 23.0 | 0.039 |
| $Clay_O$ | 34.4 | 0.090 |

280 [a]Surface area calculated from the BET equation
281 [b]Total pore volume determined from the amount adsorbed at $P/P_o = 0.99$
282

283 The distribution of the pore diameters was obtained using the BJH method based on a

284 discrete analysis of the adsorption branch of the isotherm, from which average pore

285 diameters equal to 3.8 and smaller than 6 or 18.6 nm were estimated for $Clay_F$, $Clay_O$ and

286 $Clay_{MA}$, respectively.

287 These values confirm a mesoporous structure typical of the clays originated by

288 interparticle voids, and therefore depends on the properties of the formed aggregates,

289 which in turn depend on the properties of the particles that compose them. However, the

290 presence of particles with a broad size distribution could lead to the formation of an

291 irregular mesoporous structure, with a broad pore size distribution, which in turn

influences the surface area values. Moreover, the particular layered structure of clays

293 should be considered. The assembly of clay platelets into successive structures (tactoids

294 and aggregates) is affected by the clay mineral properties, in terms of platelet-platelet

295 bonding energy, size, packing order, and alignment, leading to more or less rigid

296 aggregates, also characterized by a different order degree (Bencheqroun et al., 2019a;

297 Jiang et al., 2019; Moore and Reynolds, 1997).

298 Clay$_{MA}$ was modified by introduction of copper or zinc in order to enhance the catalytic

299 behavior of the pristine clay. The composition of all clays was determined by ICP-OES

300 analysis, with Si, Al, and Fe as the most important elements. Ca, K, Ti, and Mg, typical

301 elements of clay materials as well, were also quantified (Table 2).

302

303 **Table 2.** ICP-OES results (wt% of metals) of the pristine clays and the two

304 metal-containing Clay$_{MA}$ samples.

| Sample | Si (wt%) | Al (wt%) | Na (wt%) | K (wt%) | Mg (wt%) | Ca (wt%) | Fe (wt%) | Cu (wt%) | Zn (wt%) | Ti (wt%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Clay$_{MA}$ | 27.06 | 12.05 | 0.25 | 3.68 | 1.86 | 3.69 | 5.40 | - | - | 0.51 |
| Cu-Clay$_{MA}$ | 27.60 | 11.35 | 0.28 | 2.61 | 0.58 | 0.23 | 4.55 | 0.43 | - | 0.43 |
| Zn-Clay$_{MA}$ | 27.39 | 11.31 | 0.31 | 2.87 | 0.63 | 0.33 | 4.33 | - | 0.32 | 0.46 |
| Clay$_F$ | 23.88 | 5.93 | 0.62 | 1.47 | 1.72 | 11.44 | 3.98 | - | 0.35 | 0.29 |
| Clay$_O$ | 26.43 | 9.89 | 0.31 | 2.52 | 0.96 | 0.35 | 6.45 | - | - | 0.50 |

305

306 Clay$_{MA}$ and Clay$_O$ contain higher amounts of Fe (5.40 and 6.45 wt.%, respectively),

307 whereas Clay$_F$ is richer in calcium (11.44 wt.%), in agreement with EDX analysis. These

308 differences in composition justifies the different colours of the clays (Fig. 1). The

309 presence of iron in the pristine clays is expected to enhance the catalytic properties of

310 these materials for Fenton reactions. Furthermore, the presence of various metals such as

In the case of $Clay_{MA}$, the introduction of Cu or Zn leads to a remarkable decrease in the

Ca and Mg contents (about 90 and 70%, respectively); a more limited variation is instead

observed for K, Fe, and Ti, whose contents decrease by about 20, 30, and 15%,

respectively. The decrease in the content of the metals present in the original clay,

especially observed for Ca and Mg, is reasonably due to an ion exchange process

involving such cations and those contained in the aqueous solution of the Cu or Zn

precursor nitrates (i.e., $Cu^{2+}$ or $Zn^{2+}$, and $H^+$).

All these samples were analyzed by XPS to determine the composition, the relative

distribution, and the oxidation state of the components present on the surface. In

agreement with ICP-OES analysis, the predominant elements in all the recorded survey

XPS resolution spectra are oxygen (O 1s), carbon (C 1s), iron (Fe 2p), silicon (Si 2p), and

aluminum (Al 2s), typical for clay minerals (Elmi et al., 2016). In addition, small amounts

of potassium (K 2p), calcium (Ca 2p), and sodium (Na 1s) were also detected. The binding

energies (BE) of the principal elements as well as their surface amounts (wt%) are

reported in Table 3.

**Table 3.** Binding energies (BE) and the amount of the elements (wt%) obtained from the
XPS resolution spectra in the C 1s, O 1s, Cl 2p, N 1s and Ag 3d regions of the
samples.

| Sample | $Clay_O$ | | $Clay_F$ | | $Clay_{MA}$ | |
|---|---|---|---|---|---|---|
| peak | BE (eV) | wt (%) | BE (eV) | wt (%) | BE (eV) | wt (%) |

| | | | | | |
|---|---|---|---|---|---|
| Si 2p | 102.56 | 24.71 | 102.96 | 27.24 | 102.73 | 23.75 |
| Al 2s | 119.26 | 9.24 | 119.46 | 7.42 | 119.53 | 10.04 |
| O 1s | 531.76 | 50.59 | 532.06 | 51.33 | 532.03 | 49.96 |
| C 1s | 285.06 | 5.30 | 285.06 | 6.77 | 285.13 | 6.60 |
| Fe $2p_{1/2}$ | 724.36 | 1.96 | 725.76 | 1.72 | 725.83 | 1.37 |
| Fe $2p_{3/2}$ | 711.76 | 1.99 | 712.66 | 1.33 | 711.93 | 1.76 |
| Fe 3p | 56.14 | 2.03 | 56.25 | 1.01 | 55.91 | 1.58 |

It can be noted that the BE values are similar for all the elements irrespective of the pristine clay. By converse, some differences exist between the clays in the surface concentration of the different components, which are linked to the geological deposits where these materials came from. In particular, the surface amount of iron is in the order $Clay_O$ (5.98 wt%) > $Clay_{MA}$ (4.71 wt%) > $Clay_F$ (4.06 %). The comparison with the chemical analysis results (Table 2) shows similar Fe contents both on the surface and in the bulk, indicating that it is homogeneously distributed throughout the clays particles. The energy separation ($\Delta E$) between the two peaks of Fe 2p is 12.6, 13.1 and 13.9 eV, for $Clay_O$, $Clay_F$ and $Clay_{MA}$, respectively, and the presence of the Fe 3p peak suggests the existence of iron in different oxidation states. For all clay samples, the high-resolution XPS spectra recorded in the Fe region show that both the $2p_{1/2}$ and $2p_{3/2}$ peaks visible in the corresponding survey spectra can be deconvoluted in three and four components, respectively (Fig. 3).

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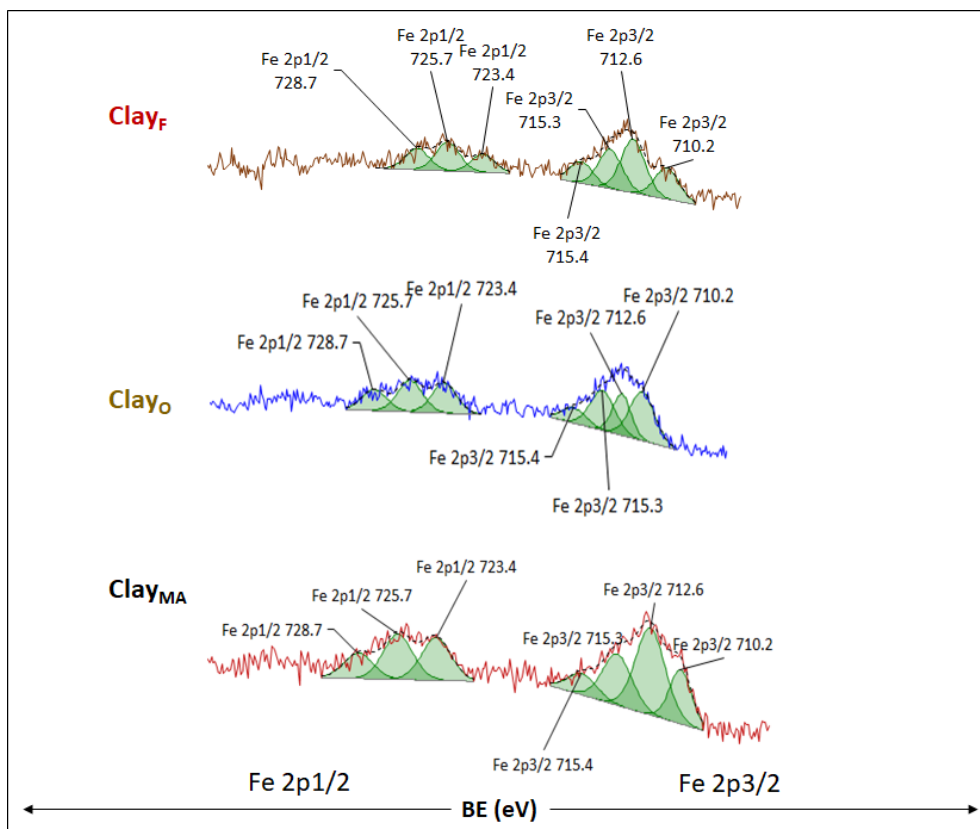
**Fig. 3.** High-resolution XPS spectra of Fe 2p of all pristine clays.

350

For all the samples, the Fe $2p_{1/2}$ peak appears to be composed by three components at 728.7, 725.7, and 723.4 eV, whereas the Fe $2p_{3/2}$ peak results from the overlapping of four contributions at BE values of 710.2, 712.6, 715.3, and 715.4 eV. These values of BE are related to the presence of $Fe^{3+}$ and $Fe^{2+}$ in the form of oxides in the clay minerals (Elmi et al., 2016; Handbook of X-ray Photoelectron Spectroscopy, 1992; Naumkin et al., 2012).

The C 1s peak at about 285 eV is ascribable to surface-atmosphere interactions or to residual precursors (Ihekweme et al., 2020; Todea et al., 2013), whereas the O 1s peak close to 532 eV is due to the elemental oxygen, oxides, oxygen in water, and metal oxides associated with the elements (Ihekweme et al., 2020). Signals of Si 2p at 103 eV and Al 2s at 119.5 eV are attributed to Si-O-Si and Si-O-Al chemical bonds, or to both atoms coordinated with other elements, typical of these type of materials (Elmi et al., 2016;

Tissot et al., 2016). Both the Si 2p and Al 2s peaks can be deconvoluted in three components, as shown in their high-resolution XPS spectra (Fig. S2). For Si 2p, the presence of these three contribution in all clays suggests that Si atoms are tetrahedrally coordinated with oxygen by Si-O-Si and Si-O-Al, which confirms the presence of such bonds in these materials (Elmi et al., 2016). In addition to those of Al 2s, Al 2p peaks were identified at about 74 eV for all the pristine clays. The presence of the three components for the Al 2s signal and the appearance of the Al 2p peak close to 74 eV suggest the existence of the same coordination than for Si and the presence of Al-OH bonds where aluminum is in tetrahedral and octahedral coordination. From the literature, the binding energy values of Al 2p in the simultaneous presence of tetrahedral and octahedral Al atoms are intermediate between the binding energy values of octahedrally and tetrahedrally coordinated species (Elmi et al., 2016). Thus, the BE values at 74.14, 73.25, and 74.91 eV for $Clay_O$, $Clay_F$, and $Clay_{MA}$, respectively, suggest that Al atoms at the clays surface have tetrahedral or/and octahedral coordination (Fig. S2).

Samples obtained by modifying $Clay_{MA}$ with Cu or Zn were also analyzed by XPS. Concerning the major components, their XPS profiles were similar to that of the pristine clay. The BE regions of Cu 2p and Zn 2p were also investigated to have information about the nature and the surface concentration of the metals. Peaks of Cu $2p_{1/2}$ and Cu $2p_{3/2}$ were detected at 953.48 eV and 931.98 eV, respectively, from which a Cu surface amount of 0.47 wt% was calculated. Likewise, in the XPS spectrum of Zn-$Clay_{MA}$, two peaks ascribable to Zn $2p_{1/2}$ and Zn $2p_{3/2}$, respectively, were identified at 1041.11 eV and 1025.21 eV, which allowed of determining a Zn surface content of 0.34 wt%. Noteworthy, both the Cu and Zn concentrations on the surface are similar to those determined by ICP-OES analysis for the bulk (Table 2), which suggests a homogeneous distribution of the metals throughout the $Clay_{MA}$ particles.

388    The XRD pattern of the raw clay from Fez (Clay$_F$) is presented to exemplify the

389    identification of the detrital and clay minerals present in these materials (Fig. S3). This

390    sample also contains non-clay minerals, typically detrital minerals like quartz, mica, and

391    plagioclase (< 2 mm). However, the presence of reflections at 3.86, 3.04, and 2.50 Å even

392    in the clay size fraction < 2 µm (oriented aggregates) indicates that calcite is the most

393    abundant non-clay mineral. Illite is indicated by the values for $d_{001}$ of 10.1 Å and $d_{002}$ of

394    5.02 Å, which are not influenced by EG-solvated conditions. Kaolin mineral, probably

395    kaolinite, was identified by the $d_{001}$ and $d_{002}$ reflections at 7.06 Å and 3.59 Å, respectively.

396    Moreover, chlorite is detected by the 00l reflections around 7.00 Å, 4.74 Å, and 3.55 Å

397    (Moore and Reynolds, 1997). Regarding smectite, it was identified combining the

398    patterns of air-dried samples with those of the glycolated and heated ones. Thus, the broad

399    reflection in the region of low-2θ, at 15.87 Å for the air-dried sample, is expanded to

400    approximately 17 Å for the EG-solvated. After heating, this peak collapses to 10 Å, which

401    is characteristic of the smectite mineral phase. Iron oxyhydroxide goethite is present in

402    trace amounts, as indicated by a weak, but typical reflection at 2.69-2.70 Å. As Clay$_F$,

403    Clay$_O$ also contains illite and kaolin mineral, but the other phases are interstratified

404    vermiculite-chlorite, and goethite.

405

**3.2 Fenton-like reaction of the dyes**

407    The choice of the oxidation reaction is reliant on the nature of the pollutants and their

408    stability in Fenton-like reaction. The Fenton reaction is distinguished by the combination

409    of ferrous salts and hydrogen peroxide, culminating in the generation of hydroxyl radicals

410    ($^{\bullet}$OH) that swiftly drive the decomposition of pollutants (Assila et al., 2023a; Assila et

411    al., 2023b; Fu et al., 2022; Wang and Tang, 2021). Notably, clays contain a significant

412    iron content, which plays a crucial role in promoting degradation through the Fenton

Concerning the pollutants, they were chosen due their presence in aqueous effluents in Morocco. Congo Red (CR) and Tartrazine (Tar) are azo molecules, di and mono, respectively, while caffeine (Caf) is a purine molecule based in an xanthine core with two fused rings, a pyrimidinedione and imidazole, in which the three methyl groups are located at positions 1, 3, and 7 (Fig. S4). Azo molecules are more easily oxidized than the purine molecules by Fenton reaction (Assila et al., 2023a; Assila et al., 2023b; Fu et al., 2022; Wang and Tang, 2021).

Tar and Caf were studied by a typical Fenton-like reaction with all the pristine clays. Moreover, in order to improve the efficacy of the degradation of these pollutants, two new heterogeneous catalysts were prepared with $Clay_{MA}$ by the introduction of copper ($Cu-Clay_{MA}$) or zinc ($Zn-Clay_{MA}$).

The catalytic results obtained with the different heterogeneous catalysts for the degradation of Tar and Caf through Fenton-like reaction, using the experimental conditions determined in (Assila et al., 2023a), are displayed in Fig. 4 and 5. Blank runs were also made in the presence of only hydrogen peroxide or raw clays. Hydrogen peroxide by itself was unable to degrade the dyes; indeed, only 4 % of conversion was determined after 5 h of reaction. Similarly, the adsorption tests showed that the clays were able to remove less than 3 % of the dyes after 5 h of reaction. These results suggest that the simultaneous presence of $H_2O_2$ and clays is required to successfully remove dyes from aqueous media through the Fenton-like reaction.

Fig. 4 displays the results for Tar and Caf degradation in terms of both pollutant's conversion and TOC, after 5 h of reaction in the presence of the clay catalysts.
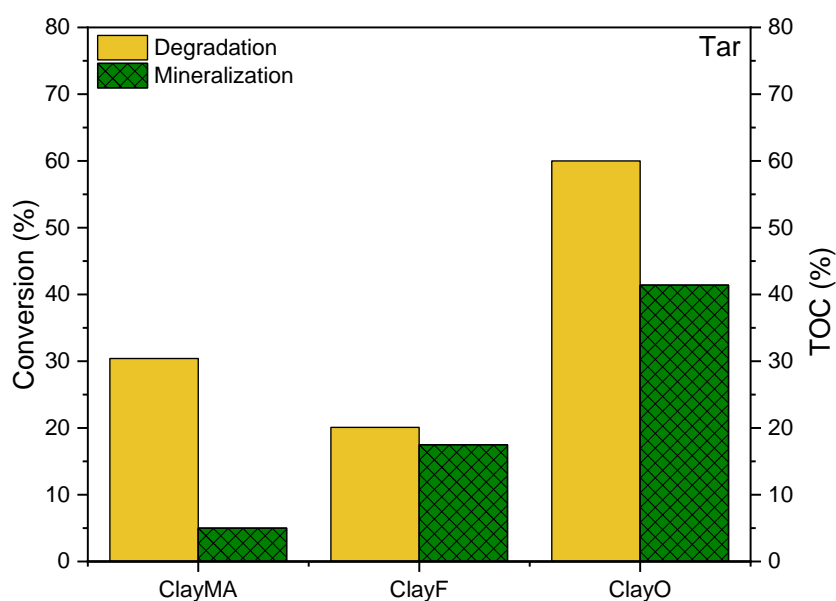
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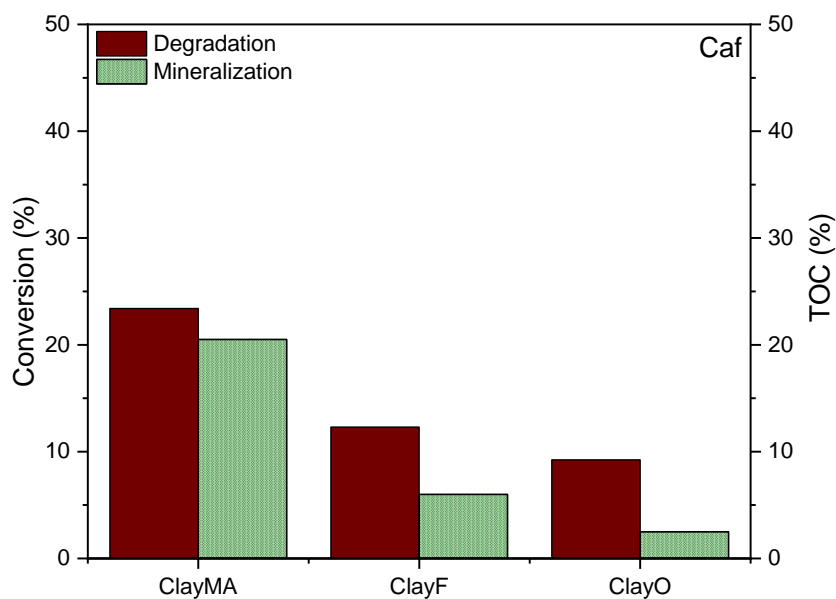


438
439 **Fig. 4**. Conversion and TOC percentages after Tar and Caf degradation by Fenton-like

440 reaction in presence of Clay$_{MA}$, Clay$_F$, and Clay$_O$. Reaction conditions: 250 mL of dye

441 solution (30 ppm); 5 mL of H$_2$O$_2$ solution (90 mM); T = 40 °C; pH = 3.0; 0.2 g of catalyst.
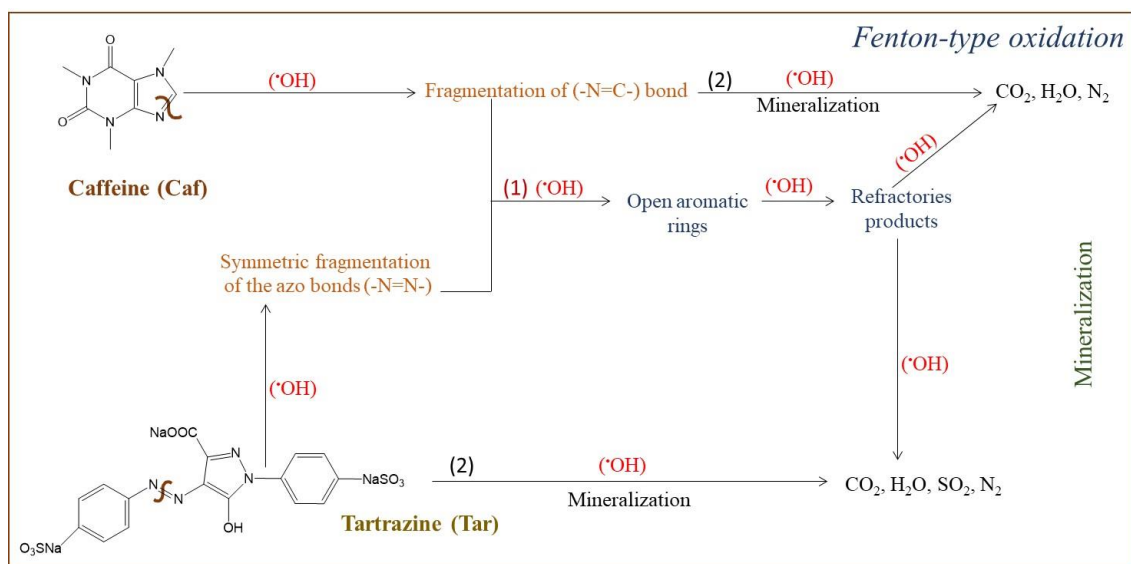
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All clays are more effective in degrading Tar than Caf, with $Clay_O$ showing the best performance, achieving in the case of Tar 60 % of conversion and 41.5 % of mineralization. This suggests that the catalyst can favor the formation of hydroxyl ($^\bullet$OH) radicals responsible for Tar degradation. On the other hand, $Clay_{MA}$ and $CLay_F$ show a much lower removal capacity, reaching conversion values of 30.5 and 20.1 %, respectively. Notably, although the conversion is higher for $Clay_{MA}$, the degree of mineralization for this catalyst is only 5 %.

In the case of Caf degradation, the behavior of the clay catalysts are different, with $Clay_{MA}$ being the best one with 23.4 % of conversion. The low values obtained for Caf conversion in the presence of the raw clays confirm that the caffeine molecule is very stable, and these catalysts are not able to fully convert the pollutants initially present (30 ppm), despite the better mineralization degree for $Clay_{MA}$ (20.5 %), followed by $Clay_F$ (6 %) and $Clay_O$ (2.5 %). These catalytic results are not only dependent on the molecular structure of the pollutants but also to the chemical composition and the geological place of the clays. For Tar degradation, a clay rich in iron at the surface ($Clay_O$, Fe = 5.98 wt%) enhances the Fenton-like reaction ($Clay_O$), followed by $Clay_F$ which has a homogeneous distribution of iron with higher amount of calcium (Tables 2 and 3).

To investigate the effect of Zn or Cu addition on the catalytic behavior of $Clay_{MA}$, the Fenton-like reaction was studied using both Zn-$Clay_{MA}$ and Cu-$Clay_{MA}$ as heterogeneous catalysts for the removal of both dyes. The pertinent results are compared with those obtained for the pristine clay in Fig. 5.

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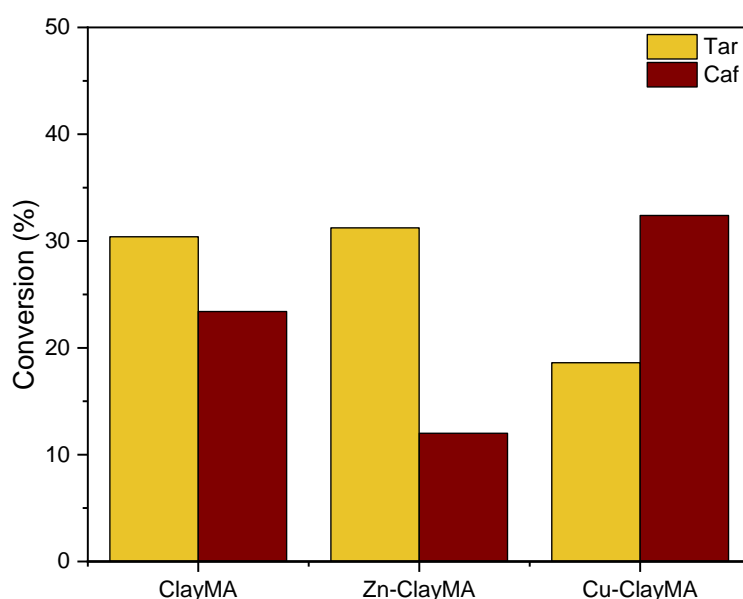
**Fig. 5**. Conversion of Tar and Caf by Fenton-like reaction in the presence of Clay$_{MA}$, Zn-

Clay$_{MA}$, and Cu-Clay$_{MA}$. Reaction conditions: 250 mL of dye solution (30 ppm); 5 mL of

H$_2$O$_2$ solution (90 mM); T = 40 °C; pH = 3.0; 0.2 g of catalyst.

468

Zn-Clay$_{MA}$ and Clay$_{MA}$ have the same behavior for Tar conversion, which suggest that

the presence of Zn does not improve its degradation. In addition, the presence of copper

leads to worst performance. By converse, for Caf degradation the presence of copper

improves the oxidation of the molecule (32.4 %) compared to the pristine clay, the pristine

clay, whereas the presence of Zn is detrimental for the catalyst, which loses its activity.

From the catalytic results obtained for the Fenton-like reaction, the best catalysts turned

out to be the raw clay from Ourika region (Clay$_O$) and the Cu-Clay$_{MA}$ sample for Tar and

Caf degradation, respectively.

The stability of Clay$_O$ in the Fenton-like oxidation of Tar was studied by performing two

reaction-regeneration cycles and the same catalytic behavior was observed. In addition,

after each reaction test, the amount of leached metals was measured by ICP-OES and no

493

**Fig. 6.** Proposed mechanism pathways for Fenton-like degradation of Caf and Tar

molecules.

Being not stable in the acidic medium used in the Fenton-like reaction because of its precipitation, the Congo red (CR) dye degradation was instead performed through the electro Fenton-like reaction, using $Clay_F$ and $Clay_O$ modified electrodes. In our previous work, CR was degraded using Fe-zeolite modified catalysts based on different zeolite structures (Bencheqroun et al., 2022c). In that case, the Fe-(H)ZSM-5 modified catalysts showed the best degradation results due to the acidic properties of the MFI structure (Bencheqroun et al., 2022c).

The cyclic voltammmetry studies between -2.0 V and +2.0 V *vs.* SCE potential with the clay-modified electrodes based on $Clay_O$ and $Clay_F$ on Carbon Toray (CT) were performed with a scan rate of 50 $mVs^{-1}$ in the presence of NaCl as electrolyte or with the CR dye (25 ppm), at room temperature (Fig. 7).
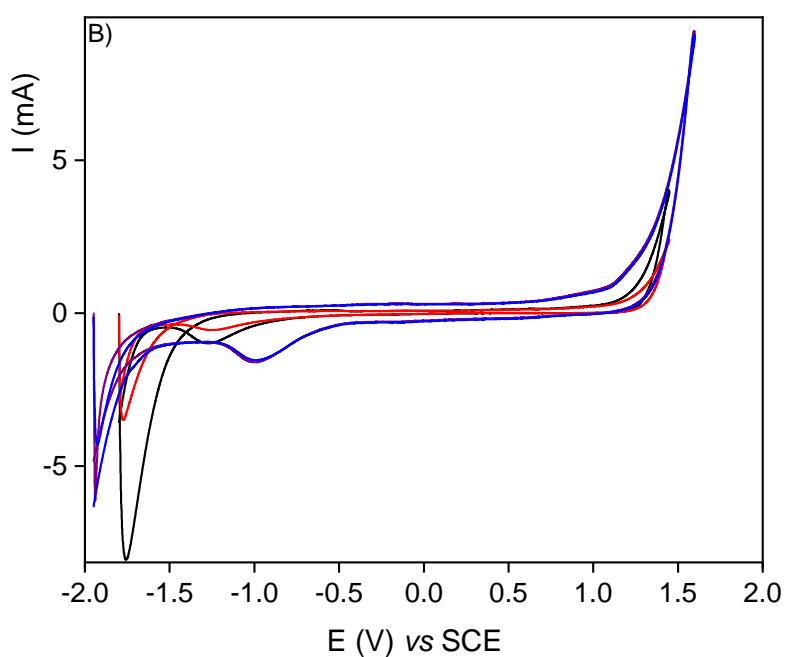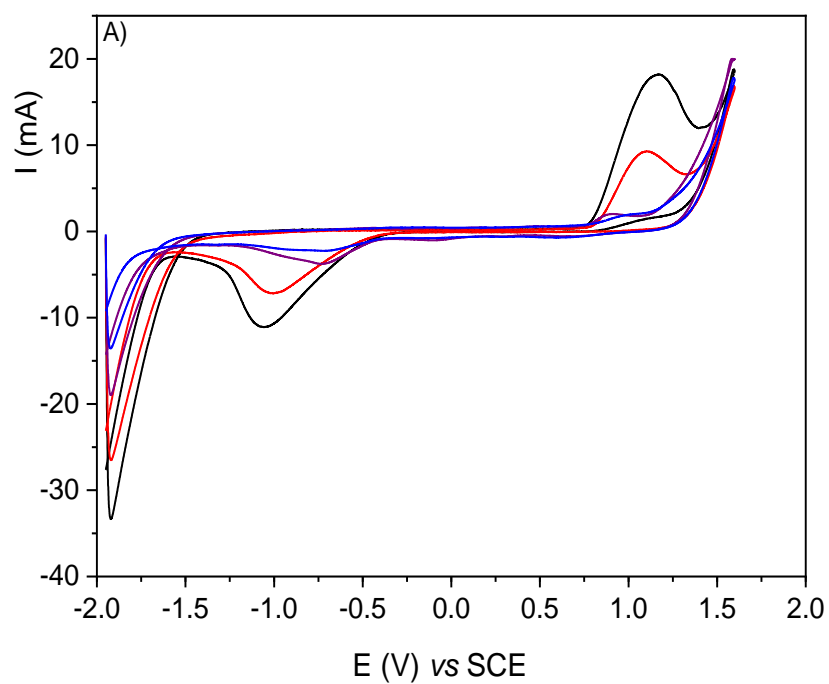
Fig. 7. Cyclic voltammograms of the CME based on: A) $Clay_F$ and B) $Clay_O$ at a scan rate of 50 mVs$^{-1}$, in the absence of dye (black and red curves) and in the presence of 25 ppm of CR (blue and violet curves) in NaCl (0.10 M).

521

The electro behavior of the CME are different and it is probably related to the presence of different iron species, *i.e.* the Fe(II)/Fe(III) couple, or other cations present on the surface of both clays, as determined by ICP-OES and XPS analyses (Tables 2 and 3). The Clay$_O$-modified electrode in the absence of CR dye (black and red curves) shows one irreversible cathodic process at -1.3 V *vs.* SCE in 0.1 M NaCl medium. For the raw clay from Fez City, an anodic redox process is observed at 1.2 V *vs.* SCE, and in the reverse scan of the potential, a reduction peak can be seen at -1.0 V *vs.* SCE.

In the presence of CR dye (blue and violet curves), both CME are active and show an increment in the anodic process, attributed to the catalytic activity of the catalysts. The oxidation of CR starts at 0.8 V and 1.1 V *vs.* SCE for Clay$_F$ and Clay$_O$, respectively, after the oxidation of Fe(II) into Fe(III), indicating that the presence of Fe(III) species on the electrode surface is necessary for the oxidation of this organic dye (Bencheqroun et al., 2022c).

The rate-determining step of the CR oxidation process can be determined by voltammetry studies, where the slope of the logI (mA) *vs.* v (mVs$^{-1}$) curves in 0.1 M NaCl medium corresponds to 0.62 and 0.55 to Clay$_F$ and Clay$_O$, respectively. These values are consistent with a kinetic of the electrochemical reaction governed by the diffusion step (Bencheqroun et al., 2022c).

The electrolysis of CR (50 ppm, 0.072 mM) with CME was performed with an applied potential of 2.0 V *vs.* SCE, at room temperature, without hydrogen peroxide. Both clays-CME are efficient in degrading the dye by electro Fenton-like reaction, but Clay$_F$ is more effective since it removes the dye in less time of reaction than Clay$_O$. Fig. 8 shows the results obtained for Clay$_F$-modified electrode in the beginning and after 2 h of reaction, as well as the evolution of the CR conversion.

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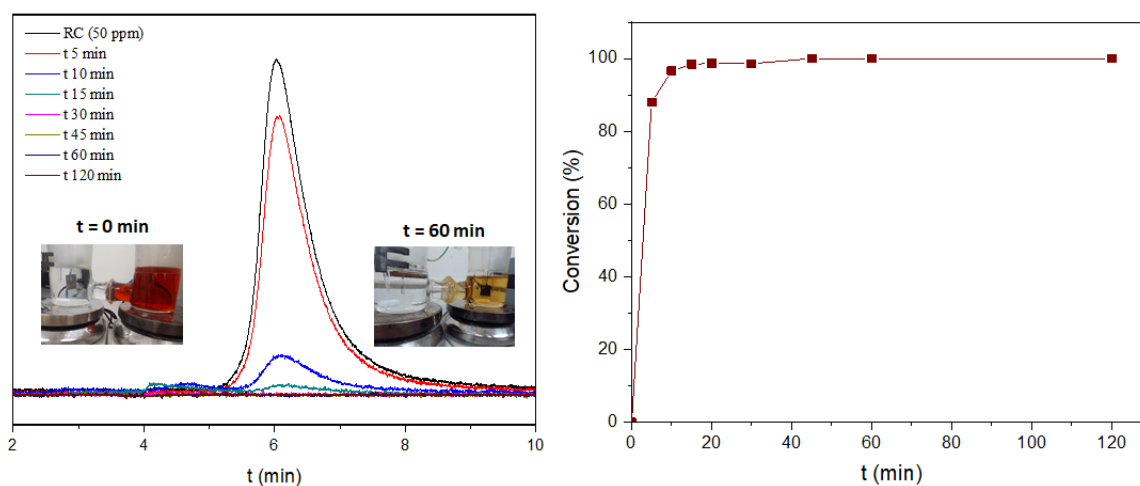
**Fig. 8.** HPLC-UV/vis chromatograms and the conversion of CR (■) *vs.* electrolysis time for the electroxidation of CR in the presence of Clay$_F$-modified electrode.

The results show that degradation occurs very fast since 81 % of the CR molecule is degraded after 5 min, being fully oxidized after 45 min of reaction (Fig. 8). At the end of reaction (2 h), TOC was determined and 67 % of mineralization was calculated. A similar value of mineralization (64 %) was previously obtained with the best Fe(H)ZSM5-modified electrode (Bencheqroun et al., 2022c). However, on the Clay$_F$-modified electrode, CR degradation appears to be faster than on the electrodes modified with Fe-MFI zeolites, on which only 74 % of conversion was achieved after 10 min of reaction (Bencheqroun et al., 2022c).

HPLC-UV/vis and ionic chromatographic (IC) analyses were employed to quantify the products at the end of reaction. The results reveal the presence of sulfate ions and several low molecular weight carboxylic acids, which are the byproducts of the CR rings opening triggered by the hydroxyl radicals produced during the electro-Fenton reaction (Fig. 9 and Table 4).
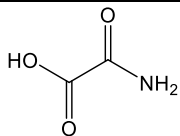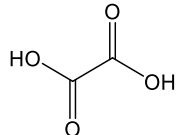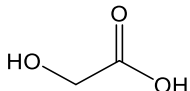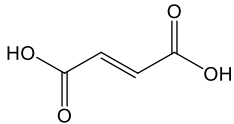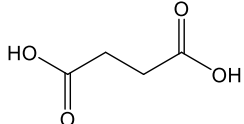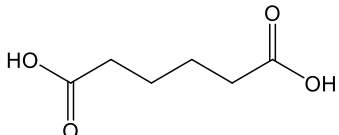
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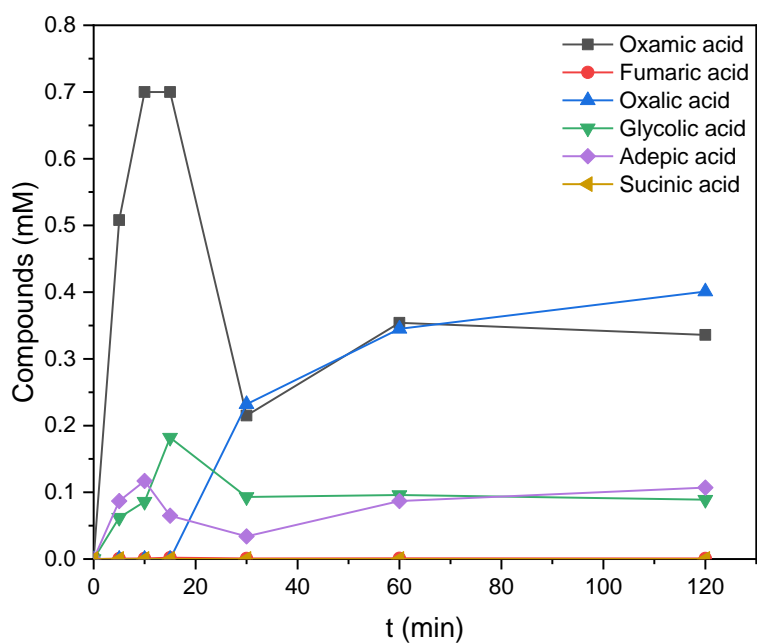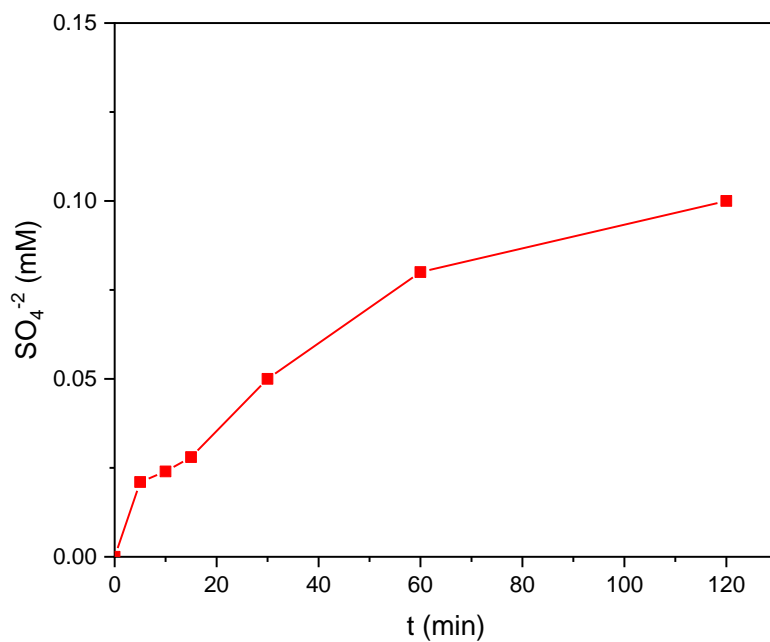
**Fig. 9.** The evolution of the compounds and sulfate ions during the electrolysis of CR in

presence of CME based in Clay$_F$.

567

**Table 4.** Identification of the byproducts

| Byproduct | | Concentration (mM) | Percentage (%) |
|---|---|---|---|
| Oxamic acid | | 0.336 | 36 |
| Oxalic acid | | 0.401 | 43 |
| Glycolic acid | | 0.089 | 9.5 |
| Fumaric acid | | 0.011 | <0.1 |
| Succinic acid | | $0.5 \times 10^{-5}$ | <0.01 |
| Adepic acid | | 0.117 | 11.5 |

569

570 The major compounds identified at the end of electrolysis were oxamic, oxalic and adipic

571 acids, and sulfate ions. These recalcitrant products result from the degradation of the dye

572 by the electro-generation of the oxygenated radical species and the presence of Fe(III)-

573 hydroperoxo species. These species come from the oxidation of water in the adopted

574 oxidative conditions since oxygen is produced at 2.0 V *vs.* SCE (Bencheqroun et al.,

575 2022c). The higher mineralization rate (67 %) determined for $Clay_F$-CME is probably

576 related to the chemical composition of this raw clay as well as the geological place. As

577 mentioned before, this clay is rich in calcium and has a homogeneous distribution of iron,
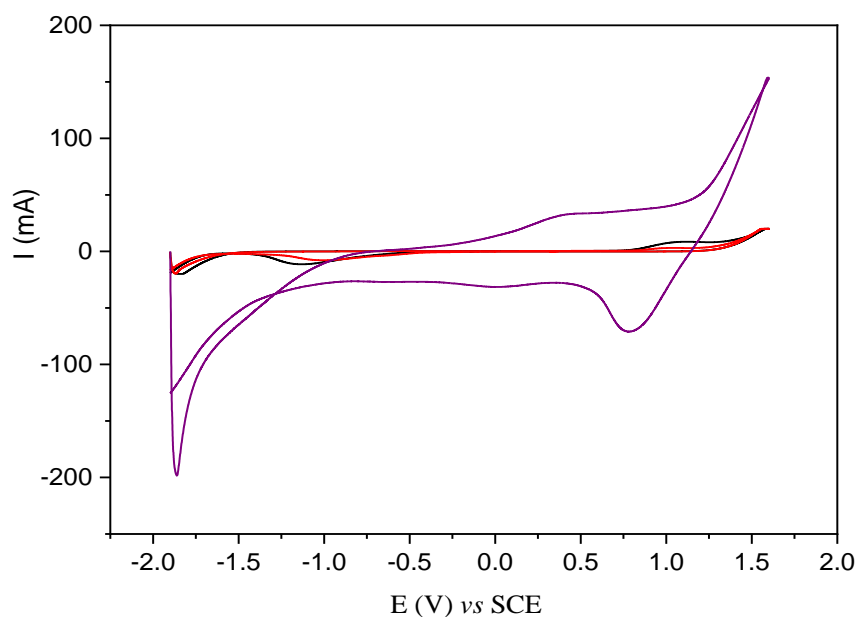
578 which enhance the electro-Fenton reaction.

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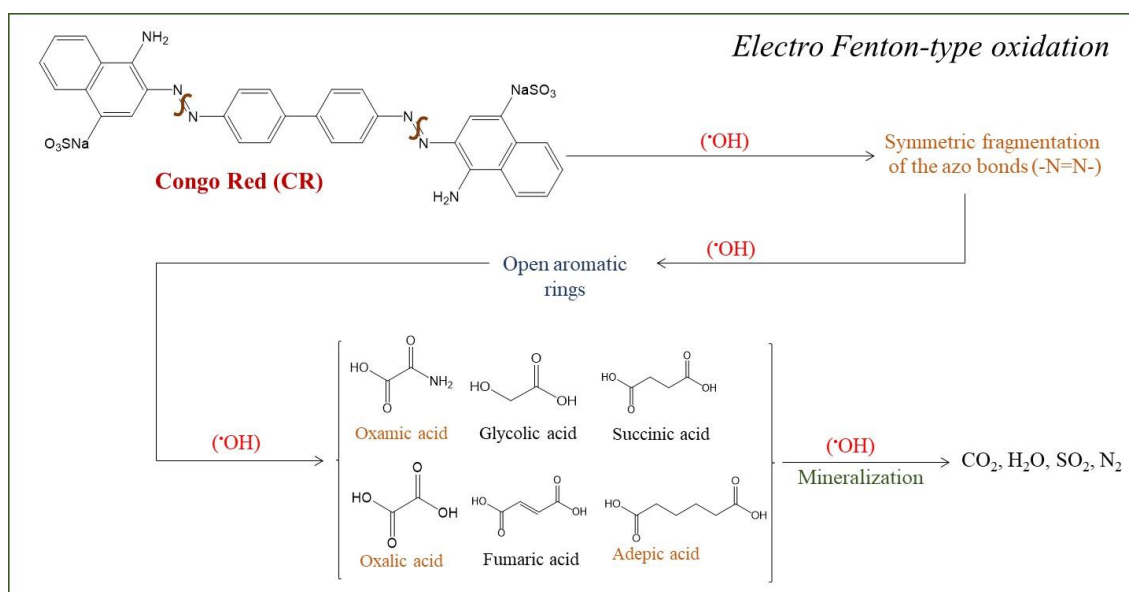


**Fig. 10.** Proposed mechanism pathway for electro-Fenton reaction of CR.

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590

591    **Fig. 11.** Cyclic voltammograms of CME based on Clay$_F$, recorded at 50 mVs$^{-1}$ before (red

592    and black curves) and after the electrolysis (violet curve) of Congo Red dye (0.072 mM)

593    in NaCl (0.10 molL$^{-1}$).

594

595    After electrolysis, an increase in the overall current intensities was observed, which is

596    attributed to the restructuring of the electrode surface, including an increase in the active

597    surface, due to the oxidative treatment during electrolysis. This increase may also be due

598    to the contribution of current intensities resulting from the oxidation of some electrolysis

599    products. This behavior prove the stability of the CME based on Clay$_F$. The same behavior

600    was observed after the electrolysis of CR with zeolite.

601

602    **4. Conclusion**

603        In this study, the Fenton-like reaction was used as the oxidative process for

604    degrading two organic pollutants (Tar and Caf), using three raw clays from Morocco as

605    heterogeneous catalysts. Under the adopted experimental conditions, these clays are more

effective in oxidizing tartrazine than caffeine. The best catalytic results were obtained in the presence of Clay$_O$ and Clay$_{MA}$, with 60.0 and 23.4 % of conversion, and 41.0 and 20.5 % of mineralization for Tar and Caf, respectively. The introduction of zinc or copper into Clay$_{MA}$ does not lead to a significant improvement in the degradation of Tar, the conversion of the metal-containing clay being equal to that of the starting one. However, Cu-Clay$_{MA}$ enhances the oxidation of the caffeine molecule (32.4 %) compared to the pristine clay. Moreover, the electro-Fenton-like reaction was found to promote the oxidation of CR at room temperature with a high mineralization degree (67 %), avoiding the use of redox agents. Our study shows that the raw clays from Morocco can be successfully applied in water treatments as a low-cost heterogeneous catalyst for a sustainable process.

**Conflicts of interest**

There are no conflicts of interest to declare.

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