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ABSTRACT

Commercial carbon felt (CF) substrates have been modified with iron-rich MFI zeolite nanoseeds prepared by a solvothermal microwave-assisted synthesis method. The as-prepared material (MFI@CF) was characterized by TGA, XRD, SEM, and used as both cathode and catalyst in heterogeneous electro-Fenton (EF) process for the abatement of a biorefractory model dye pollutant, Acid Orange 7 (AO7). The complete degradation of 200 mL AO7 (0.1 mM) was achieved after 40 min contact with the modified material instead of more than 120 min with the pristine one. The proposed catalytic system exhibited an attractive activity with the total organic carbon (TOC) removal reaching 26.6 % after 8 hours at pH 6.5. The present results prove a promising efficiency of iron-rich MFI@CF material for a “green” EF treatment of water

pollutants, avoiding the use of any non-recyclable soluble Fe^{2+} salt classically required as EF catalyst.

KEYWORDS. *Heterogeneous electro-Fenton process, Fe-MFI zeolite, Mineralization, Dye removal, Water treatment.*

1. Introduction

Water pollution leads to many serious problems that affect the entire biosphere on the planet Earth [1] [2]. Hence, the wastewater treatment for the reuse of polluted water sources remains one of the great concerns of current scientific research. Many different methods have been applied either at lab-scale or industrial scale for the abatement of water pollutants by *e.g.* adsorption [3], bacterial degradation [4], radiolytic degradation [5], filtration [6], electrodialysis technology [7] [8], *etc*. However, these methods still present several limitations related namely to the formation of secondary wastes, or production of highly toxic intermediates such as 2-naphtol or 1-amino-2-naphthol, because of low treatment efficiency [5]. To overcome these bottlenecks, Advanced Oxidation Processes (AOPs) have been developed, including diverse technologies combining *e.g.* UV-light with strong oxidizing agents like O_3 or H_2O_2 in photolysis [9], photo-Fenton by ferrioxalate-Fenton/UV-A and TiO_2/UV-A processes [10] [11] or other Fenton-based processes [12]. Among these methods, electro-Fenton (EF) process is known as an optimal approach to decompose completely the persistent organic pollutants (POPs) in aqueous media. This method involves the production of hydroxyl radicals ($^{\bullet}OH$), as powerful oxidizing agents, which can destroy and transform POPs into low toxicity compounds such as short chain carboxylic acids (formic or acetic acids) with their further mineralization into CO_2 and H_2O [13] [14]. The process involves two steps [15]:

i) Production of hydrogen peroxide from oxygen reduction:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

ii) and EF process:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

In homogeneous EF process, a soluble iron catalyst is added to the solution and regenerated through the reduction of Fe^{3+} (Eq. 3). However, adding Fe^{2+} to treated waters leads to another pollution risk for the environment because ferrous ions remain in the solution and their removal is not a trivial task. Consequently, in recent years the heterogeneous EF process has attracted a special attention as it avoids the usage of homogeneous catalyst. Hassan & Hameed proved that using Fe–ball clay (Fe–BC) as heterogeneous EF catalyst led to 99% decolorization of anthraquinone dye Reactive Blue 4 with initial concentration of 50 mg L^{-1} after 140 min treatment [16]. This catalyst was prepared from $FeSO_4 \cdot 7H_2O$ via impregnation method combined with calcination step at 500°C. In addition, pyrite has been applied commonly due to its low cost and abundance. Numerous pollutants were degraded by usage of pyrite in EF process, for example antibiotic levofloxacin [17], azo dye – the (4-amino-3-hydroxy-2-p-tolylazo-naphthalene-1-sulfonic acid) [18], or tyrosol [19]. In addition, other catalyst sources like iron alginate gel beads [20], Fe_2O_3 modified kaolin [21], γ-FeOOH [22], pyrrhotite [23] have been also successfully applied in EF process. Recently our research group has studied heterogeneous EF catalyst based on hierarchical CoFe-Layered Double Hydroxide (CoFe-LDH) synthesized by *in-situ* solvothermal method. It exhibited an outstanding stability with high TOC removal even after multiple reaction cycles [24].

In order to find other possible alternatives in the area of heterogeneous EF process, in this work we propose for the first time the application of EF system based on carbon felt (CF) substrates modified with iron-rich MFI zeolite nanoseeds prepared by solvothermal microwave-assisted synthesis method. This approach is of a particular interest because it combines the attractive properties of both CF and zeolite material. CF has been known as an effective material for EF process because of its low cost, good conductivity, high mechanical stability, porosity and

surface area which supply plentiful active redox sites [25] [26]. Concerning the zeolites, in the area of wastewater treatment, they are typically used as adsorbers taking advantage of their high specific surface areas. In addition large variety of functionalities, such as acid-base or redox centres can be incorporated into the zeolite structures to confer them catalytic properties enabling a chemical abatement of waste water. In this respect, zeolites with incorporated heteroatoms, *i.e.* Fe, could be used as heterogeneous catalyst in EF treatment of water pollutants, avoiding the use of any non-recyclable soluble Fe^{2+} salt classically used in EF process and at the same time enabling a repetitive utilisation of the system in consecutive reaction cycles.

The efficiency and stability of the cathode was investigated by the treatment of a dye solution contaminated by Acid Orange 7 (AO7) which was chosen as a model azo dye molecule. This work contributes to the development of processes for the treatment of effluents containing biorefractory pollutants in general with a particular attention devoted to heterogeneous EF process using iron-rich zeolite materials.

2. Experimental

2.1. Reagents and materials

Tetraethyl orthosilicate (TEOS, 98%), tetrapropyl ammonium hydroxide (TPAOH, 20 wt% aqueous solution), AO7 (Aid Orange 7 also called Orange II sodium salt), anhydrous sodium sulphate (Na_2SO_4, 99.0 – 100.5%), graphite powder and iron (II) sulphate hepta-hydrate ($FeSO_4{*}7H_2O$, 99%) were purchased from Sigma-Aldrich. Iron (III) acetylacetonate ($Fe(acac)_3$, 99.9%) was obtained from Alfa Aesar and sodium hydrogen carbonate ($NaHCO_3$, ≥99.5%) from ACS, Karlsruhe. The carbon felt was bought from A Johnson Matthey Co., Germany. All these reagents were used as received, without further purification.

2.2. Preparation of MFI zeolite based catalyst

The MFI zeolite based catalyst was produced according to a protocol described elsewhere (Motuzas et al. 2017). The molar concentration of the mother solution was set at (x/2) Fe_2O_3:

100 SiO_2: 40 TPAOH: 1950 H_2O: 400 C_2H_5OH, where x was adapted to the required molar amount of Fe in the MFI zeolite structure. The selected Fe-rich MFI zeolite has been synthetized from solutions having Si/Fe atomic ratio equal to 50 (2 at% Fe). It must be noted the synthesis of MFI zeolites from solutions with Si/Fe atomic ratios < 50 failed due to undesirable gelation of the reaction sols. For the sake of comparison, a pure silicalite-1 zeolite material (0 at.% Fe) has been prepared from an iron-free solution. After aging the sols for 24 h at 25 °C (under continuous stirring), they were poured in autoclaves and heated in a commercial laboratory microwave oven (Milestone ETHOS 1600). The hydrothermal treatment was conducted in two steps. First, the closed autoclaves were irradiated for 90 min at 80 °C with a microwave power of 250 W. Then the power was increased up to 400 W for heating the autoclaves up to 180 °C for 60 min. Finally, the autoclaves were cooled down to 50 °C before opening. The formed solid products were separated by centrifugation at 9500 rpm (JOUAN B4i) and washed twice with distilled water and centrifuged again. The as-washed MFI zeolite powders were dispersed in water (3.7 wt.%) and the resulting suspensions were used to impregnate the commercial carbon felts (CF). The prepared MFI@CF composite materials were dried for 4 h at 155 °C and then submitted to a calcination treatment. The calcination has been carried out under flowing nitrogen (200 $mL.min^{-1}$) in a tubular furnace (Vecstar Ltd) at 550 °C for 4 h, with heating and cooling rates of 5 °C min^{-1}. Non calcined MFI@CF composite materials were also used immediately after drying at 155 °C.

2.3. Material characterizations

Chemical and structural characterizations of the prepared materials have been performed by scanning electron microscopy (SEM, Hitachi S-4800), X-ray diffraction (XRD) (PANAlytical Xpert-PRO diffractometer equipped with a X'celerator detector using Ni-filtered Cu-radiation) and EDX analysis (Silicon Drift Detector (SDD), X-MaxN, Oxford Instrument) coupled to a Zeiss EVO HD15 SEM analyzer. The N_2 sorption-desorption isotherms were measured with a Micromeritics ASAP 2010 equipment (outgassing conditions: 200°C-12h).

2.4. Heterogeneous electro-Fenton set-up

The heterogeneous EF experiments were carried out in an open electrolytic cell with 250 mL capacity and a working volume of 200 mL. The cathode was either a commercial CF, noted as raw CF, or a composite MFI@CF material with dimensions 1 cm ∗ 2 cm ∗ 1.27 cm. The MFI@CF was prepared according to the method described in section 2.2. The anode was a Pt foil setting parallel with the cathode at a distance of 3 cm. AO7 was used as a model pollutant and its concentration was fixed at 0.1 mM for all experiments in this study. Na_2SO_4 (50 mM) was added into dye solution which plays the role of supporting electrolyte. The initial solution pH was ~ 6.4 without any adjustment with H_2SO_4 or NaOH. Homogenization of the electrolysis solution was ensured by a magnetic stirrer at 500 rpm. Compressed air was bubbled continuously into the solution, starting 10 min before the beginning of electrolysis. Solution samples were taken at regular treatment times (2 h, 4 h, 6 h and 8 h, respectively) to quantify the evolution of the mineralization degree during EF treatment, via TOC analysis on a Shimadzu TOC-L analyzer with 8-port sampler, supplied by pure oxygen at a flow rate of 200 mL min^{-1}. Calibration of the analyzer was done by automatic dilution of standard TOC solutions (potassium hydrogenophtalate) and inorganic carbon (sodium hydrogen carbonate). The decomposition of AO7 was monitored by measuring the dye absorbance at λ = 485 nm, specific wavelength for azo bond, using Spectrophotometer Jenway 6300 (Barioworld Scientific Ltd, Dunmow UK). The absorbance of this bond was proportional to the AO7 concentration, according to the Beer-Lambert law (calibration graph).

The catalyst stability was investigated by running experiments for 5 consecutive cycles. Between each cycle, the MFI@CF was well washed by distilled water (15 μΩ) and dried at 80 °C in an oven. The efficiency of treatment was evaluated by measuring the efficiency of the washed electrode for a new TOC removal experiment.

3. Results and discussion

The strategy selected for the preparation of carbon felt electrodes modified by MFI zeolite seeds (MFI@CF) involves two steps: (i) the growth of MFI zeolite nano-seeds by MW-assisted heating and (ii) the deposition of these zeolite seeds, dispersed in aqueous suspension, on commercial carbon felts. The as-prepared electrode material was used in heterogeneous electro-Fenton (EF) process for the abatement of a model dye pollutant, acid Orange 7 (AO7). The key aspects related to the efficiency of such a reaction system have been discussed hereafter together with the characteristics of the electrodes. A special focus was devoted to evidence the promising performance of iron-rich Fe-MFI@CF material, at near neutral pH, for a "green" EF treatment of water pollutants, while avoiding the use of any non-recyclable soluble Fe^{2+} salt classically required as EF catalyst.

3.1. Preparation of MFI zeolite nanoseeds

The MFI nano-seeds were prepared by a MW-assisted hydrothermal treatment, as reported elsewhere (Motuzas et al. 2017). This procedure enables, within less than 3 h, the production of MFI zeolite seeds with uniform size distribution. The SEM images in Fig. 1a demonstrate that MFI zeolite morphology is influenced by the Fe concentration. The Fe-free (0 at.% Fe) MFI zeolite seeds (S-1) feature typical MFI type crystal morphology, while the Fe-rich (FeS-1) MFI zeolite (2.33 at.% Fe in the solid, as determined by EDX analysis) exhibit aggregated microstructure forming particles without sharp edges. It must be noted that when comparing with their non-calcined analogues, calcination carried out under the nitrogen atmosphere, does not lead to any detectable change of zeolite seeds morphology, neither for S-1 nor for FeS-1 (results not shown here).

A characteristic monoclinic MFI crystal structure has been confirmed by wide angle XRD analysis for both S-1 and FeS-1 zeolite powders (Fig.1b). The slightly higher resolution of the S-1 pattern translates its higher crystallinity degree in comparison with FeS-1 in which Fe insertion slightly disturbs the construction of the MFI crystalline network. In addition it must be

noted that XRD analysis also confirmed the absence of detectable quantity of secondary phases (i.e. extra-framework particles) like iron oxides, thus suggesting that the Fe species detected by EDX analysis are mainly incorporated in the MFI particles as intra-framework species.

3.2. Preparation of MFI@CF electrodes

As described in the experimental section, the commercial carbon felts have been modified by deposition of zeolite nanoseeds, thus forming composite MFI@CF material. SEM images of both pristine and modified carbon felt are displayed in Fig.2. As in the case of pure zeolite seeds, no difference was observed when comparing the morphology of MFI@CF non-calcined and after treatment at 550°C under the nitrogen atmosphere. SEM observations confirmed a good distribution of the zeolite nanoseeds covering nearly uniformly the surface of commercial carbon felts. Previous studies on graphite felt modified by zeolite material proved that catalyst loading affects noticeably the performance of the fabricated electrode. Once the mass of NaX zeolite on the electrode increased from 0.03 g to 0.13 g, the electrochemical activity of the electrode increased by 1.5 times [27]. In the present study, the catalyst loading was strictly controlled by weighting electrode before and after modification during the preparation procedure. An optimized electrode was obtained when its mass was kept nearly constant at 55+6 wt.% zeolite loading after thorough washing to ensure that electrode was fully covered with Fe-MFI. Over this amount no more zeolite material could be deposited on the carbon felt electrode. The modification of pristine carbon felts (S_{BET} ~ 0.1 m^2 g^{-1}) with MFI zeolites led to an increase of the specific surface area by more than 600 times, thanks to the high specific surface area of zeolite nanoseeds, even before any calcination treatment (Table 1).

When the MFI@CF samples were subjected to a calcination treatment (550°C in N_2), an additional increase of their active surface area was measured (Table 1), due to the decomposition of the organic structure directing agent (SDA, TPAOH) in the zeolite channels. The required neutral N_2 atmosphere for the calcination treatment (preserving the integrity of the CF) is less

efficient than a conventional oxidation in air for a complete evacuation of the SDA decomposition species from the zeolite pores but should result at least in a detectable liberation of zeolite channels. As expected, the SDA degradation resulted in an increase of the zeolite pore volume (i.e. from 0.049 cm^3 g^{-1} to 0.057 cm^3 g^{-1} for non-calcined and calcined samples, respectively). Hence, the modification of a raw CF with zeolite seeds, followed by its calcination in N_2 atmosphere raised nearly 1000 times the specific surface area of the raw carbon cathode.

This finding has been further confirmed by TGA experiments (Fig. 3) carried out on the zeolite seeds exhibiting ~ 12wt.% loss corresponding to the removal of the organic SDA from the zeolite material. The slight weight difference ~ 0.55wt.% between the samples treated in air and nitrogen was attributed to the presence of residual carbonaceous species on/in the zeolitic material calcined in N_2 atmosphere (lower weight loss).

3.3. Removal of AO7 by heterogeneous EF process using MFI@CF electrode

The target of present study is performing the heterogeneous EF process to treat bio-refractory pollutants in neutral medium (pH ~ 6.4). The effect of pH on AO7 degradation has been carefully investigated in our previous studies about heterogeneous electro-Fenton (EF) process using Fe-based LDH catalysts [24],[28]. It was shown that working at low pH values (i.e. 2-3) led to the Fe leaching from heterogeneous catalysts, thus inducing significant drawbacks for real environmental applications during wastewater treatment in industry. In addition to undesirable iron precipitation, an alteration of industrial equipment in acidic medium is predictable as well as a required basic treatment before discharging the solutions in the environment. Similarly, working at high pH (over 7) reduces AO7 degradation efficiency because of catalyst precipitation. Therefore, in this work, the neutral pH value of initial AO7 solution was kept unchanged in all experiments. In comparison with a raw CF electrode, the higher surface area of MFI@CF electrode is expected to induce a higher quantity of H_2O_2 electrogenerated from dissolved oxygen according to Eq.1. Hence, more H_2O_2 should react with

the heterogeneous iron catalyst *via* EF process (Eq. 2) on Fe-MFI@CF electrode for the production of oxidizing hydroxyl radicals attacking the AO7 molecules and leading to their degradation. The decay kinetics of A07 was monitored by measuring the dye absorbance at the selected single wavelength λ = 485 nm, specific for azo bond. The blank tests in the absence of Fe species were carried out at the same experimental condition as with the iron-based zeolite catalyst. The complete degradation of 200 mL AO7 (0.1 mM) was achieved after 40 min contact on the Fe-MFI@CF instead of more than 120 min on the non-modified raw CF one (Fig. 4a). The AO7 removal on raw CF was explained by the anodic oxidation that occured at the Pt anode, through Eq. 4 from water oxidation [29]:

$$Pt + H_2O \rightarrow Pt(^{\bullet}OH) + H^+ + e^- \quad (4)$$

In order to evaluate the influence of anodic oxidation on the degradation of AO7, experiments were performed using Pt as both cathode and anode. As observed in Fig. 4a, the anodic oxidation led to the color removal of AO7 after 2 h. A similar result was obtained when using a raw CF cathode and a Pt anode. Additional experiments carried out with S-1@CF cathode led also to AO7 removal due to the synergetic effect of both anodic oxidation on the electrode and strong adsorption efficiency of Fe-free MFI zeolite. Nearly 46 % of AO7 was removed after 9 min by using Fe-free MFI zeolite cathode, which was 1.5 times higher than with the bare cathode (~30 %). The fastest AO7 removal, *i.e.* EF process leading to the most efficient dye elimination in aqueous medium, was observed when applying a Fe-MFI@CF cathode, thus proving the efficiency of the carbon felt cathode modification for heterogeneous EF process. The presence of iron in the zeolite framework accelerated the treatment efficiency; hence there was 69 % of the initial AO7 amount which was degraded in the same amount of time. This increase resulted from the heterogeneous EF process enabling to generate more hydroxyl radicals (•OH) which are powerful oxidizing agents able to destroy and transform quickly AO7 dye molecules [13], [14]. The interest of Fe-MFI modification is then to combine adsorption properties of the porous material with electrocatalytic properties of iron for heterogeneous electro-Fenton as

already proposed in our previous work devoted to nitrogen-doped graphitized carbon electrodes for biorefractory pollutant removal by homogeneous electro-Fenton (Le et al., 2017b). The AO7 degradation by hydroxyl radicals formed during the heterogeneous EF process followed a pseudo-first order kinetic. The apparent rate constant was determined by plotting the ln([$AO7^0$]/[AO7]) vs. time [26]. A value of 0.226 min^{-1} was obtained for the Fe-MFI@CF cathode; this value was nearly three times higher than those obtained for a MFI@CF electrode (without any Fe catalytic sites), i.e. 0.0838 min^{-1}. In the experiment with raw CF, the anodic oxidation contributed mainly for AO7 removal with a similar rate constant value of 0.078 min^{-1}. This result strongly proved the important role of heterogeneous Fe-MFI catalyst for AO7 degradation. Moreover, this conclusion was once again confirmed via measuring TOC removal (Fig. 4b). In fact, the TOC abatement reached 26.6 % after 8 hours reaction time with the Fe-MFI@CF cathode calcined in nitrogen, while the abatement value do not overpass ~5% for the raw CF cathode

As expected without any calcination step, the heterogeneous EF process yielded a negative TOC removal. It was explained by the leaching of the organic SDA (TPAOH) from the zeolite network after synthesis. The TOC removal went down to nearly – 20 % after 4 h and then gradually climbed up due to the decomposition of organics by heterogeneous radicals. As observed in Fig. 4c, the Fe-MFI@CF cathode calcined in nitrogen lost partially its catalytic activity after 5 consecutive cycles. It was blamed for the gradual loss of Fe-MFI catalyst out from the carbon electrode during EF experiments.

According to Figures 4a&b, AO7 degradation is achieved when using a relevant zeolite modified carbon felt (Fe-MFI@CF treated at 550°C under N_2 atmosphere), in hetero-EF at circumneutral pH, by a surface catalyzed process. In comparison with conventional EF systems, the large increase of performance was ascribed to (i) surface-catalysed reaction which expands the working pH window and avoids the precipitation of iron sludge appearing at neutral pH in homogenous electro-Fenton technology, (ii) improvement of H_2O_2 production due to the increase

of the electroactive cathode surface area (accessible pore volume) which allows coupling both adsorption and EF process (reactive electrochemically materials) and (iii) further improvement of the adsorption capacity after calcination of the organic template in N_2. It is also important to note that the Fe-MFI@CF cathode exhibited relatively good reusability after 5 degradation cycles, indicating that the prepared material is a promising cathode for the removal of organic pollutants by hetero-EF technology.

4. Conclusion

In this study, we have successfully prepared a novel zeolite modified electrode which is active for heterogeneous electro-Fenton (EF) process. Iron-rich MFI zeolite nanoseeds have been deposited at the surface of a commercial carbon felt (CF) thus forming a MFI@CF composite material exhibiting an attractive activity as electrode (cathode) for direct *in-situ* formation of H_2O_2 electrogenerated from dissolved oxygen. This highly reactive electrochemical material allows a coupling of both adsorption and EF process. Indeed the presence of Fe-MFI seeds with a size of 200 nm deposited on the electrodes played an essential role in the production of hydroxyl radicals as highly reactive species for the removal of organics from the aqueous media. The TOC removal reached 27 % after 8 hours at pH 6.5 in comparison with 5 % at raw electrode. The iron rich Fe-MFI@CF cathode exhibited relatively good stability after several consecutive cycles with a decrease of the catalytic activity of ~25% due to partial wash-out of the zeolite seeds. Improvement of seed anchoring on electrode surface is currently under investigation in our group, but this preliminary work is of huge interest as it clearly demonstrates the possibility to develop heterogeneous electro-Fenton process at neutral pH instead of acidic pH in traditional electro-Fenton systems. The present study contributes importantly to (i) develop novel heterogeneous catalysts for the electro-Fenton process towards industrial applications in waste water treatment; (ii) enrich the application field using designed porous materials.

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