Stabilization of zero valent iron (Fe^0) on plasma/dendrimer functionalized polyester fabrics for Fenton-like removal of hazardous water pollutant

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ABSTRACT

This study reports the synthesis, immobilization and stabilization of multiscale zero valent iron ($\text{Fe}^0 = \text{ZVI}$) particles on fibrous polyester (PET) nonwoven membrane for heterogeneous Fenton-like removal of hazardous pollutants in water. Activation of PET fiber surface by air atmospheric plasma with or without a consecutive grafting of hyperbranched poly-(ethylene glycol)-pseudo generation 5 dendrimer having hydroxyl (-OH) end group functionality created polar reactive functional groups allowing immobilization and stabilization of ZVI particles. Synthesis of ZVI was carried through chemical reduction of ferric ions, either

through a single step in-situ, or a two-step ex-situ reduction-immobilization method. The nonwovens were characterized using wettability, Fourier transform infrared spectroscopy (FTIR), optical microscopy, scanning electron microscopy (SEM), X-ray energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA). Results confirmed the formation and immobilization of nano to sub-micronic multi-scale ZVI particles. The particle size, distribution and stability of ZVI were found to be influenced by the methods of ZVI synthesis and PET surface activation used. The ZVI particles initially formed, quasi-instantaneously turned to yellowish brown indicating the formation of oxide layer, except in the case of dendrimer grafted PET, where higher content (22.30%) and stability of ZVI was detected. All ZVI immobilized nonwovens exhibited high effectiveness towards Fenton-like degradation of malachite green dye (20 ppm), with fastest color removal (98% in 20 min) achieved by dendrimer/ex-situ nonwoven. This nonwoven could be used up to eight repeated cycles providing low TDS (52 ppm) and high COD reduction (66.23%). Combined use of eco-friendly plasma and dendrimer grafting, provides efficient fibrous textile base heterogeneous catalysis.

Keywords: Air atmospheric plasma; dendrimer; zero valent iron; polyester nonwoven; Fenton; wastewater treatment.

1. INTRODUCTION

Recently, owing to the rising scarcity of fresh water, reuse and recycling of wastewater by removal of hazardous substances is considered as a global concern [1]. The presence of colorants in water streams are of highest concern for biodiversity as well as human health due to their high toxicity, chemical stability, bioaccumulation and their resistance to conventional treatment methods [2]. Malachite green (MG) is one of the most commonly used colorants in dyeing of various textile fibres such as cotton, silk as well as in paper, ink and leather industries [3]. MG has direct effect on aquatic life, if discharged into fresh water stream it causes harmful effects in liver, intestine, gill, kidney and gonads [4, 5].

During last few decades, water researchers have introduced several methods for removing pollutants from water [6-8]. Among various physical [8], chemical [9], biological [10], and electrochemical [11] techniques, Fenton-like removal [12, 13] has been considered very effective due to the high range of applicability and superior degradation ability [14]. However, homogeneous Fenton process containing free iron ions and hydrogen peroxide has some critical disadvantages that limit its commercial application: the need of acid pH and further neutralization and separation of iron sludge in the end, is a costly and time consuming procedure [15-19].

Heterogeneous Fenton technology using various types of catalysts such as zero valent iron ($ZVI=Fe^0$) [20-23], goethite ($-FeOOH$) [24, 25], and Fe_3O_4 [26-28], has been extensively studied for pollutant degradation processes. This is considered as cost-effective system that can be useful for a wide range of practical applications. Solid zero valent iron allows reduction in iron use, and thus reduces the concentration of iron in treated water, with the potential prospect to work in an operational pH. Lejin Xu et al. [18] reported that, zero valent iron based Fenton-like system provides better degradability of phenolic compounds even in working pH condition. In recent years, nanoscale zero valent iron has been reported to be a great alternative for the treatment of various contaminants in water [29-32]. However, considerable improvement is still necessary due to unsatisfactory activity, especially the tendency to lose activity easily by agglomeration, leaching and limited reusability due to easy oxidation [31].

Heterogeneous catalysis, through immobilization of ZVI may come across as an appropriate remediation for these problems. Several researchers introduced different immobilization techniques for durable deposition and sustainable applicability. These include, layer by layer [33], adsorption [34], crosslinking [35], atomic layer deposition [36] etc. Various materials such as zeolites, clays, fibrous textiles [37-39] and inorganic-organic materials [40] have been applied as supports for metallic nanoparticles in diverse catalytic reactions [41-43]. Up to now,

these materials have attracted much attention due to their availability and effectiveness towards potential applications, particularly in the field of catalysis [44-47]. Interestingly among all those materials, special features of porous materials are necessary for use as an ideal supporting matrix for metal nanoparticles including ZVI [48-50]. Higher porosity of the support material leads to better exchanges [31, 51-54]. However, toxic binding chemicals are often used to immobilize iron particles on supporting porous materials. These chemicals remain leftover as secondary pollutants after the use of catalysts [55]. So, it is important to immobilize iron on a carrier using an eco-friendly method such as the atmospheric plasma treatment and use a carrier that can be available at a reasonable cost and easily separable from the treated water without being contaminated.

Polyester (PET-Polyethylene terephthalate) nonwoven is a readily available porous recyclable material with high porosity, low-pressure drop, and high mechanical strength. Besides, PET is non-toxic, cheap and biocompatible, as well as resistant to most acids, oxidizing agents, microorganisms and chemical reagents [56]. Due to its porous structure and high surface area, PET nonwoven has been successfully used for immobilization of various enzymes [57] and metal nanoparticles [53, 58-61] and it demonstrated to have increased stability and to allow mobility of materials. Makoto Ikegami et al. [59] described that gold catalysts supported on PET nonwoven fabric can effectively oxidize CO and remove HCHO in air. Our previous work [58] shows effective incorporation of Cu-NPs and Ag-NPs on pre-activated PET nonwoven for catalytic application. However, no study has been carried for the immobilization of Fe^0 (ZVI) particles on PET nonwovens for Fenton-like removal of pollutants in aqueous solution. Eco-technology (plasma) was introduced as eco-friendly surface activation method for PET fibre surface as a replacement of toxic binding chemicals [55]. Our previous studies describe the effectiveness of air-atmospheric plasma treatment for surface activation of PET by introducing hydroxyl $-\text{OH}$ and carboxylic $-\text{COOH}$ terminal groups [62-65]. Plasma activated PET nonwoven contains a large amount of oxygen-

containing groups on the fibre surface, which can be quite effective for the adsorption of heavy metal, such as Fe particles [66]. Higher oxygen containing polymers such as dendrimers can provide further adsorption of Fe particles proving their eco-friendliness and ability to form complexes via molecular encapsulation, covalent and non-covalent interactions [67]. Paul L. Carr et al. [68] once introduced aryl ester dendrimer/PET blends in terms of structure property characterization. However, no study addresses the use of dendrimers for immobilization of zero valent iron particles on PET nonwoven.

In this study, micro/nano scale zerovalent iron particles were effectively immobilized for the first time on a plasma treated/dendrimer grafted PET nonwoven and the stability as well as catalytic property in Fenton-like degradation of malachite green dye was investigated. The specific objectives of this study were a) immobilization and stabilization of micro/nano scale ZVI particles on pre-activated polyester nonwoven and their characterization by means of FTIR, SEM, EDS, TGA, XRD, and optical image analysis; b) evaluation of catalytic property of ZVI immobilized PET nonwovens in Fenton-like degradation of toxic malachite green dye. The mechanism of the catalytic properties improvements and reusability of the catalyst have been discussed on the basis of the materials structure, stability, and the kinetics.

2. EXPERIMENTAL

2.1 Chemicals

Hyperbranched G5-PEG10k-OH dendrimer ($C_{764}H_{1406}O_{414}$), hydrogen peroxide (H_2O_2), ferric trichloride ($FeCl_3 \cdot 6H_2O$), sodium borohydride ($NaBH_4$), ethanol (C_2H_6O), petroleum ether and malachite green dye were purchased from Sigma Aldrich Ltd. All chemicals were of analytical grade and used as received without any further purification. Deionized water used in all experiments was obtained using a water purification system provided by GFL mbh Ltd at ENSAIT, France.

2.2 Nonwoven

The nonwoven structure is based on a web of cylindrical PET fibres (average diameter 12 μm) formed by carding and consolidated by hydroentanglement (entangling with water jets). It was manufactured at the European nonwoven platform, CENT (Tourcoing, France). The nonwoven used had the following characteristics: thickness of 950 μm , an areal density of 230 g/m^2 , a porosity of 93 %, and an air-permeability of 645 mm/sec .

The PET fibrous nonwoven was cleaned to be free from surface impurities and spinning oil as described in our previous work [69]. The cleanliness of the PET samples was checked by measuring the surface tension of final rinsing water (used to clean the PET samples), which remained constant and equal to 72.6 mN/m , which is indeed the surface tension of pure water.

Plasma treatment of PET nonwoven

Air atmospheric plasma treatment was used to activate the PET surface using a ‘Coating Star’ plasma treatment set-up provided by Ahlbrandt System (Germany). The nonwoven sample was placed between two electrodes, which when subjected to a potential difference, created a glow discharge called the ‘Dielectric Barrier Discharge’ (DBD)[69]. Atmospheric air was chosen as gas, and the following parameters were used, a frequency of 26 kHz, inter-electrode distance of 1.5 mm, and a plasma treatment power of 60 kJ/m^2 , was used to treat the nonwoven on both sides.

Dendrimer grafting on the plasma treated PET nonwoven

Hyperbranched poly-(ethylene glycol)-pseudo generation-5 dendrimer having hydroxyl (-OH) end group functionality was grafted onto plasma treated PET nonwovens through chemical sorption [58]. Typically, 1 g of plasma treated nonwoven was impregnated in 1:3 (vol.) water-ethanol mixtures containing 0.30 g of dendrimer at 75 $^{\circ}\text{C}$ for 5 h. The resulting products were filtered, washed and then dried overnight at room temperature.

2.3. Immobilization of ZVI particles on PET nonwovens

Two pathways, in-situ and ex-situ methods were used for ZVI particle immobilization on plasma treated PET nonwovens (with or without dendrimer grafting) - as shown in scheme 1.

(i) **In-situ method** consists of a single step with simultaneous synthesis and immobilization of ZVI as described in scheme 1(iii-iv). An aqueous solution was prepared by dissolving 0.02 g of ferric chloride (0.2 wt %) ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 75 mL distilled water and then 1 g of pre-activated PET nonwoven was dipped in the solution under vigorous stirring, and subsequently 5 mL of NaBH_4 (0.04 M) solution were added, and the mixture was stirred vigorously for 30 min at 25 °C. Upon addition of NaBH_4 , the colour of the solution turned from yellow to black, indicating the reduction of the iron ions and in-situ formation of zero valent particles, consistent to our previous study [14]. Afterwards, the mixture was stirred for 4 h at 75 °C. The resulting nonwoven material was recovered from the solution followed by mild wash with deionized water and dried overnight in a vacuum dryer at room temperature.

(ii) **Ex-situ method** consists of a two-step synthesis and immobilization method as illustrated in scheme 1(v-viii). Here, 1 g of pre-activated PET nonwoven was dipped in 75 mL of aqueous ferric chloride solution and stirred vigorously for 4 h at 75 °C. After that, the nonwoven was removed from the ferric solution and rinsed. Subsequently when NaBH_4 (0.04 M) solution (5 mL) was dropped onto the nonwoven gradually, the porous material immediately turned black (Scheme 1 (vii-viii)). The NaBH_4 solution was dropped until there was no hydrogen gas (as bubbles) indicating complete reduction of ferric iron to zero valent iron as described in our previous works [60, 70]. The resulting ZVI immobilized PET nonwovens were dried overnight in a vacuum dryer at room temperature.

2.4. Methods for characterisation of nonwovens before and after ZVI immobilization.

2.4.1. Wettability measurements (water contact angle [$\theta_{\text{H}_2\text{O}}$] and capillary uptake)

Wettability measurements were carried out before and after activation with air atmospheric plasma and dendrimer grafting to quantify the degree of hydrophilisation of the nonpolar PET surface. For water contact angle $> 90^\circ$, contact angle of a sessile water droplet deposited at the nonwoven surface was observed and measured using optical microscopy. A wicking test was equally used for capillary uptake measurements and for water contact angle $< 90^\circ$. A tensiometer from GBX instrument (France) was used to investigate the capillary uptake of the activated PET nonwovens as well as to calculate the water contact angle more precisely. A rectangular-shaped (size 3 cm x 5 cm) PET nonwoven sample was mounted vertically on the weighing position of the tensiometer. After that, the PET nonwoven was brought down into the contact with static deionized water. As soon as the lower part of the nonwoven touched the water surface, movement of the nonwoven was stopped. Immediate changes in weight due to meniscus formation and weight of the water entrapped inside the nonwovens were noted and water contact angle was calculated using equation (1).

$$W_m \times g = \gamma_L \times \cos \theta \times \rho \quad (1)$$

Here, (W_m) is calculated meniscus weight, (g) represents gravitational acceleration, (γ_L) is the surface tension of water and (ρ) symbolizes sample perimeter of nonwoven in contact with the liquid.

2.4.2. Microscopic analysis

A digital optical microscope (diamond scientific ltd., China) and a scanning electron microscopy (SEM, JEOL JSM IT100, JEOL Ltd., Japan), were used for analyses the surface of the nonwovens at each step of functionalization. Prior to SEM, samples were sprayed with a conducting resin followed by sputter coating with carbon films having a chunkiness of ~10 nm. The LEO Ultra 55 was used for high resolution imaging equipped with an EBSD (electron backscattered diffraction) detector for grain orientation and texture analysis.

2.4.3. Superficial analysis of functionalized nonwovens

FTIR was used to characterize samples before ZVI immobilization, while EDS (mounted on SEM) was used both before and after ZVI immobilization. XRD was also used to characterize the type of iron species immobilized on the fiber surface.

Fourier transform IR spectroscopy (FTIR) was carried out using a Tensor 27 (Bruker) spectrometer with a ZnSe ATR crystal. The samples were drilled before IR analysis, and background spectra were recorded on air.

Energy dispersive spectroscopy (EDS) analysis was carried out using BRUKNER axes EDS analyzer mounted with JEOL JSM IT100 SEM (described above).

X-ray diffraction (XRD) analysis was carried out using Diffractometer Siemens D5000, equipped with Cu source (45kV, 40mA), Göbel mirror on a primary side and long Solar slits and Sol'X energy dispersive detector on secondary side. Sample was rotating and a grazing-incidence geometry was used with incident beam fixed at 10 degrees, step size 0.05 degrees was used with 4 seconds per step.

2.4.4. Quantifying particle size and distribution of iron

Quantitative percentage of immobilized iron per surface area of nonwoven was carried using EDS-SEM while iron particle size and distribution was carried using image analysis software ImageJ 1.40G (<http://rsb.info.nih.gov/ij/download.html>). A randomly selected particles were observed using high definition SEM images and analyzed for each sample to obtain the average size of the particles, standard deviation and size distribution histograms.

Thermogravimetric analysis (TGA) was used to quantify the weight% of iron for each nonwoven using a thermogravimetric analyzer (TG-DTA, A6300R. It was carried at various temperatures ranging from 25 °C to 800 °C in nitrogen (N₂) medium where the rate was 10 °C/min. It was performed to investigate the weight changes associated with decomposition,

oxidation, and any other physical or chemical changes that result in sample weight loss or gain.

2.4.5. Catalytic degradation of malachite green by ZVI on PET nonwovens

The catalytic performance of ZVI immobilized PET nonwovens (1 cm²) for heterogeneous Fenton-like degradation of MG (malachite green) dye in presence of hydrogen peroxide (H₂O₂) was investigated at room temperature, using UV/Visible spectrophotometer along with TDS and COD analysis.

UV/Visible spectrophotometer

Color removal was monitored using UV/Visible spectrophotometer. In a typical reaction, a MG aqueous solution (2.5 mL, 20 mg/L) was mixed with H₂O₂ (0.5 mL, 0.3 M) solution. The instant-to-initial absorbance ratio of MG solution (A_t/A_0) was measured at different time intervals. Thus, changes in A_t/A_0 allowed to assess the progress in color removal. The color removal or conversion percentage was calculated according to the concentration at predetermined time intervals by using equation (2) [33].

$$\text{Conversion \%} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

Here, C_0 is the initial concentration of pollutants, and C_t represents the concentration of pollutants at different time intervals during catalytic degradation.

Reusability analysis

After completion of degradation of MG, the nonwovens with immobilized ZVI were removed from the solution and washed with distilled water before reuse for another degradation cycle. Samples were tested to evaluate their potential re-use in catalysis system under the same experimental conditions.

Total dissolved solids (TDS) analysis

Toxicity reduction as well as to quantify the rate of loss of ZVI into water from the functionalized nonwovens, the TDS was measured by using Hanna Instruments pH, EC, TDS

Combo Tester (HI98129 Hanna Instruments Ltd. USA). Principally, this device estimate the quantity of TDS by measuring the electrical conductivity of the water by passing a small current through it. The meter displays the TDS value in parts per million (ppm).

Chemical oxygen demand (COD) analysis

Chemical oxygen demand analysis was carried out using COD vials provided by CHEMetrics, Inc. (USA) following “ASTM D1252-06-chemical oxygen demand (dichromate oxygen demand) of water” test method B. Typically, COD measures the oxidizable organic matter content of a wastewater sample. The samples reacted with an acidic solution of potassium dichromate in the presence of a catalyst and digested for 2 h at a temperature of 150 °C. Oxidizable organic compounds reduce the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) to the chromic ion (Cr^{3+}). In the COD kits, the decrease in dichromate ion was measured calorimetrically at $\lambda_{620 \text{ nm}}$. The test results are expressed as the number of milligrams of oxygen consumed per liter of sample (mg/L COD) using equation (3) [71].

$$\text{COD (mg/L)} = (23010 * A_{620}) - 3 \quad \dots\dots\dots (3)$$

Here, A_{620} is the absorption of the COD solution at $\lambda_{620 \text{ nm}}$ after digested with the sample solution for 2 hours at a temperature of 150 °C.

Scheme 1: Pathways used to immobilize ZVI on nonwoven PET, after plasma treatment (i) and dendrimer grafting (ii) through in-situ (iii or iv) and ex-situ (v -vii or vi -viii) reduction method. [Yellow spheres represent iron (III) ions, orange spheres represent ZVI with iron oxides shell, and black spheres represent ZVI].

3. RESULTS

Table 1 summarizes the description and terminology of all samples studied in this work.

Table 1: Terminology of PET nonwoven samples

Sample description	Terminology
PET nonwovens (without ZVI immobilized)	
Polyester nonwoven (before plasma activation)	PET nonwoven
Plasma treated PET nonwoven	PN
Dendrimer grafted on plasma treated PET nonwoven	PN@Dr

PET nonwovens (ZVI immobilized)

ZVI on plasma activated PET using in-situ method	In-PN-ZVI
ZVI on plasma activated PET using ex-situ method	EX-PN-ZVI
ZVI on plasma activated + dendrimer grafted PET using in-situ method	In-PN@Dr-ZVI
ZVI on plasma activated + dendrimer grafted PET using ex-situ method	EX-PN@Dr-ZVI

PART 1- Analysis of functionalized nonwovens before and after ZVI immobilization***3.1 Analysis of surface activated polyester nonwoven membrane, using plasma and dendrimer grafting******3.1.1. Wettability analysis***

Water contact angle (θ_{H_2O}) and capillary uptake are parameters determining wettability of nonwovens and hence reflect the fibre surface energy and diffusion resistance of the nonwoven, before and after pre-activation of polyester fibre surface. Figure 1 and table 2 show optical images of sessile water droplet deposited at the nonwoven surface, and capillary uptake before and after plasma activation and dendrimer grafting. Water contact angle was as high as 141° at the surface of untreated PET nonwoven, which is higher than that of PET fibre surface ($\theta_{H_2O} = 80^\circ$). The high surface roughness due to irregularities of the nonwoven surface would account for such a high water contact angle. Upon activation of the nonwoven with plasma and/or dendrimer grafting, the droplet was immediately absorbed (see Figure 1a),

and θ_{H_2O} calculated from the meniscus weight [equation (1)] was 0° for both PN and PN@Dr nonwovens.

Figure 1: Wettability analysis using (a) sessile water droplet for θ_{H_2O} measurement and (b) capillary uptake using wicking test

No capillary uptake was recorded for untreated nonwoven (234 mg meniscus weight were recorded). However, upon surface activation by using plasma treatment and dendrimer grafting, capillary uptakes increased up to 1453 mg and 1650 mg, respectively. Plasma treatment leads to increased wettability due to scissions of ester bonds present at the PET fibre surface, yielding hydrophilic terminal carboxyl and hydroxyl ends as confirmed in our previous studies [69]. Decreased water contact angle (0°) of the outer nonwoven surface and increased capillary uptakes confirm the increased wettability of PET fibre surfaces both at the outer surface and in the inner core of the nonwovens. The further increase in capillary uptake

to 1650 mg with hyperbranched dendrimers indicates the influence of additional hydrophilic groups introduced onto the PET surface upon successful dendrimer grafting with hyperbranched G5-PEG10k-OH dendrimers, containing numerous hydrophilic –OH (hydroxyl) terminal groups.

3.1.2. Surface morphology

The morphological structures of nonwovens before and after surface activation were observed by scanning electron microscopy as shown in figure 2. The untreated PET nonwoven (Figure 2a) exhibit a network of randomly overlapping fibers with a fairly smooth surface. SEM pictures show no change in surface morphology after plasma treatment (Figure 2b). However, irregular patches can be observed at the fiber surface of PN@Dr nonwoven (Figure 2c), probably due to the presence of dendrimer branches at the fiber surface. These patches appear as irregularly shaped layered clusters as shown in scheme 2. The functional groups present on treated PET nonwovens were further characterized by *EDS X-Ray* and infrared analysis (see following sections).

Figure 2: SEM images of PET nonwoven (a), PN (b), and PN@Dr (c)

Scheme 2: SEM images of fibre surface of PN@Dr and schematic illustration of scale aggregates of dendrimer on plasma activated PET fibre.

3.1.3. Surface analysis

EDS X-ray energy dispersive spectroscopy

SEM analysis was further validated by the X-ray energy dispersive spectroscopy analysis based on atomic identification and their ratio obtained from atom percentage analysis as summarized in table 2, obtained from corresponding EDS spectroscopy (see Figure S1 in supplementary information). The atomic ratio O/C was 0.35 for the untreated PET nonwoven and it increased to 0.38 after plasma activation and can be due to the incorporation of additional oxygen atoms following ester bond scissions and creation of carboxylic and hydroxyl terminal groups. A further increase in O/C ratio (0.43) was observed in PN@Dr, due to increase of hydroxyl (-OH) groups present in the dendrimer grafted PET nonwovens

Table 2: Wettability and atomic identification analysis of activated PET nonwovens

Samples		θ_{H_2O}	Capillary uptake	Atomic identification	
		(°)	in180s (mg)	(EDS analysis)*	
PET	nonwovens	141	-	C atom %	O atom %
(untreated)				65.33	34.77
				O/C = 0.35	

PN (treated by air	0	1453	C atom %	O atom %
atmospheric plasma			62.13	37.87
treatment)			O/C = 0.38	
PN@Dr (treated by	0	1650	C atom %	O atom %
air atmospheric			57.02	42.98
plasma and			O/C =0.43	
dendrimer grafting)				

*Atoms peak regions: Carbon (C, 0.278 keV), Oxygen (O, 0.550 keV)

Fourier transform infrared spectroscopy

The FTIR spectra of polyester surface after air atmospheric plasma treatment and dendrimer grafting are illustrated in figure 3. The untreated and activated PET nonwovens demonstrated some bands in the region $1750\text{-}650\text{ cm}^{-1}$, which were attributed to the stretching vibration of CH_2 , C=O , aromatic C=C and C-O of ester, indicating the structure of polyester fibers [72] [73]. Visible changes were seen in the double peaks at 2850 and 2920 cm^{-1} assigned to stretching vibration of O-H from carboxylic acid [74]. The intensities of these double peaks increase after plasma treatment compared to the untreated PET, but decrease after dendrimer grafting. There are increased carboxylic acid groups after ester bond scissions by plasma treatment, however as these groups interact with OH -hydroxyl groups of dendrimers, their peak intensities are lowered.

The large peak which is characteristics of PEG (dendrimer) and which generally appears at 3440 nm [75], does clearly visible in the case of PET with dendrimer grafting, most probably due to the non-homogenous deposition of the dendrimer. These appear as patches, on plasma activated PET fiber surface as observed in the SEM images (see Figure 2c).

Figure 3: FTIR spectra of untreated, air atmospheric plasma treated and dendrimer grafted polyester nonwoven

3.2. Analysis of ZVI immobilized polyester nonwoven

After morphological analysis using optical microscopy and SEM, iron particle size and distribution analyses were carried using image analysis software ImageJ 1.40G. Quantification of immobilized iron per surface area of nonwoven fiber surface was carried using EDS-SEM. The atomic ratios, Fe/O and Fe/C, as well as the % weight of iron-based particles for each nonwoven were determined by thermogravimetric analysis (TGA). Finally, XRD was used to characterize more precisely; the type of iron species immobilized on the fiber surface.

3.2.1. Morphological properties

Images from optical and scanning electron microscopes (see Figure 4) show observable morphological changes occurring after ZVI immobilization. Indeed during ZVI formation and immobilization, blackish nonwovens were obtained in all cases, which however turned readily to yellow-brownish color in contact with air, especially in the case of nonwovens without dendrimer grafting. Ex-PN-ZVI and In-PN-ZVI nonwovens are thus yellowish brown. However, Ex-PN-ZVI (Figure 4d) has a more intense yellowish brown coloration than the In-PN-ZVI nonwoven (Figure 4a).

In the case of dendrimer grafted nonwovens In-PN@Dr-ZVI (Figure 4g) and Ex-PN@Dr-ZVI (Figure 4j), in addition to iron particles fixed at the fiber surface; blackish spherical shape micro-size iron particles are seen entrapped within the pores of the nonwoven, inside the fiber webs. The PN@Dr-ZVI looks more yellowish brown while the Ex-PN@Dr-ZVI is black colored.

The iron particle size distributions are illustrated in figure 5. Without dendrimer, almost spherical shaped iron particles are distributed on the overall PET fiber surface (see Figure 4b-f). These particles range from 50 to 400 nm in the case of In-PN-ZVI (Figure 5a-b) and up to 700 nm for the Ex-PN-ZVI (Figure 5c-d). The modal value for iron particle size is between 100-200 nm for both nonwovens. In the case of In-PN-ZVI, the deposit is fine and more homogeneous while with Ex-PN-ZVI, thicker, assorted deposits of larger iron particles appear on the fiber surface.

On the dendrimer grafted PET nonwovens as shown in figure 5e-f and figure 5g-h, iron particles within the same size range (up to 600 nm) appear but these do not cover the entire fiber surface (see Figure 4g-i). They seem localized, just like dendrimers are on the fiber surface. The localized agglomeration of particles iron can be due to strong crosslinking property of dendrimers that stabilized the zerovalent iron particles on the nonwoven fiber surface. The black spherical shape iron particles entrapped within the pores of these dendrimer grafted nonwovens have a size of $25 \pm 5 \mu\text{m}$ (see optical microscope images). They appear at the intersections of fibers where iron nanoparticles from each fiber grow and merge to form micro-sized iron particles.

Figure 4: Morphological analysis of ZVI immobilized PET nonwovens; (a, b,c):optical , SEM and high magnification image of In-PN-ZVI ; (d,e,f): optical , SEM and high

magnification image of Ex-PN-ZVI ; (g, h, i): optical , SEM and high magnification image of In-PN@Dr-ZVI ; (j, k,l): optical , SEM and high magnification image of Ex-PN@Dr-ZVI.

Figure 5: Analysis of iron particle size and distribution analyses using high resolution SEM and image analysis software ImageJ ; (a, b) In-PN-ZVI, (c, d) Ex-PN-ZVI, (e, f) In-PN@Dr-ZVI and (g, h) Ex-PN@Dr-ZVI.

3.2.2. Identification and quantification of immobilized iron

Quantification of immobilized iron per surface area of nonwoven was carried using EDS-SEM, and the Fe/O and Fe/C ratios determined, while the weight% of iron with respect to nonwoven weight determined by thermogravimetric analysis (TGA). Whereas the precise nature of iron particles immobilized in the nonwovens was identified by XRD analysis.

EDS X-ray analysis

Spectral analysis (Figure 6) showed that, in addition to two peaks (0.278 keV and 0.550 keV), corresponding to carbon and oxygen atoms, two more apparent characteristics peaks at 0.725

keV and 6.432 keV assigned to iron (Figure 6b) were recorded. Atomic ratio analysis obtained from EDS demonstrates the quantitative significance of iron particles; (see Table 3), with the lowest iron content of 18% for In-PN-ZVI and the highest content of 27% for Ex-PN@Dr-ZVI nonwoven.

Atomic ratios Fe/C and Fe/O were found to be 0.33 and 0.79 respectively for In-PN-ZVI, and 0.52 and 1.30 for Ex-PN@Dr-ZVI, indicating a substantial content of immobilized iron particles.

Longer time for iron particle growth during the ex-situ immobilization combined with the formation of larger-micro-size iron particle formation on dendrimer grafted PET, would lead to the highest iron content in the Ex-PN@Dr-ZVI nonwoven.

Figure 6: Characteristics EDS analysis of PET nonwovens (a) before and (b) after ZVI immobilization.

Thermogravimetric analysis (TGA)

TGA of ZVI immobilized nonwovens allowed to evaluate thermal stability of nonwovens and carry out a quantitative analysis of iron particles incorporated onto the PET nonwovens. Upon incorporation of ZVI particles, thermal stability of PET fibers improved as shown in figure 7. Several mass loss regions were located at around 350–500 °C and 500–800 °C.

For ZVI immobilized on the dendrimer grafted PET, additionally mass loss was detected around 60-150 °C most probably due to evaporation of superficial water in the nonwovens. The mass loss region located around 360–450 °C is attributed to the thermal degradation of the PET polymer, which is alike for all samples [76]. However, recorded divergent residual mass values indicate the dissimilar amount of iron deposited on each sample.

Table 3 shows the weight% of iron/weight of nonwoven, with the lowest weight% observed for In-PN–ZVI (13.26 %), and the highest for Ex-PN@Dr-ZVI (24.7 %). Higher amount of iron incorporation by the ex-situ reduction and dendrimer grafting method as detected by SEM-EDS, was confirmed by TGA analysis.

However, dissimilar iron content values were detected by TGA compared to SEM-EDS for the In-PN@Dr-ZVI and the ex-situ Ex-PN@ZVI nonwovens have. Indeed, surface scanning by SEM does not evaluate properly the iron content of micro-size iron particles immobilized in the inner depth of the dendrimer grafted nonwovens. TGA analysis allows a more precise measurement of iron content.

Figure 7: Thermogravimetric analysis of PET nonwovens, (a) PN, (b) PN@Dr, (c) In-PN-ZVI, (d) Ex-PN-ZVI, (e) In-PN@Dr-ZVI and (f) Ex-PN@Dr-ZVI.

Table 3: Quantitative analysis and size of ZVI immobilized PET nonwoven.

Samples	(EDS-SEM analysis)* <i>Atomic identification per scanned surface</i>	Weight % of immobilized iron on nonwovens (g /100 g of nonwoven) [%] **	Dimensions of ZVI particles												
In-PN-ZVI	<table> <tr> <td><i>C</i></td> <td><i>O</i></td> <td><i>Fe</i></td> </tr> <tr> <td><i>atom %</i></td> <td><i>atom %</i></td> <td><i>atom %</i></td> </tr> <tr> <td>57.23</td> <td>23.96</td> <td>18.81</td> </tr> <tr> <td colspan="3"><i>O/C = 0.41, Fe/C = 0.33, Fe/O = 0.79</i></td> </tr> </table>	<i>C</i>	<i>O</i>	<i>Fe</i>	<i>atom %</i>	<i>atom %</i>	<i>atom %</i>	57.23	23.96	18.81	<i>O/C = 0.41, Fe/C = 0.33, Fe/O = 0.79</i>			13. 26	(170 ± 55) nm
<i>C</i>	<i>O</i>	<i>Fe</i>													
<i>atom %</i>	<i>atom %</i>	<i>atom %</i>													
57.23	23.96	18.81													
<i>O/C = 0.41, Fe/C = 0.33, Fe/O = 0.79</i>															
Ex-PN-ZVI	<table> <tr> <td><i>C</i></td> <td><i>O</i></td> <td><i>Fe</i></td> </tr> <tr> <td><i>atom %</i></td> <td><i>atom %</i></td> <td><i>atom %</i></td> </tr> <tr> <td>56.0</td> <td>21.69</td> <td>22.30</td> </tr> <tr> <td colspan="3"><i>O/C = 0.38, Fe/C = 0.40, Fe/O = 1.02</i></td> </tr> </table>	<i>C</i>	<i>O</i>	<i>Fe</i>	<i>atom %</i>	<i>atom %</i>	<i>atom %</i>	56.0	21.69	22.30	<i>O/C = 0.38, Fe/C = 0.40, Fe/O = 1.02</i>			15.1	(190 ± 86) nm
<i>C</i>	<i>O</i>	<i>Fe</i>													
<i>atom %</i>	<i>atom %</i>	<i>atom %</i>													
56.0	21.69	22.30													
<i>O/C = 0.38, Fe/C = 0.40, Fe/O = 1.02</i>															
In-PN@Dr-ZVI	<table> <tr> <td><i>C</i></td> <td><i>O</i></td> <td><i>Fe</i></td> </tr> <tr> <td><i>atom %</i></td> <td><i>atom %</i></td> <td><i>atom %</i></td> </tr> <tr> <td>57.20</td> <td>21.72</td> <td>21.06</td> </tr> <tr> <td colspan="3"><i>O/C = 0.38, Fe/C = 0.37, Fe/O = 0.97</i></td> </tr> </table>	<i>C</i>	<i>O</i>	<i>Fe</i>	<i>atom %</i>	<i>atom %</i>	<i>atom %</i>	57.20	21.72	21.06	<i>O/C = 0.38, Fe/C = 0.37, Fe/O = 0.97</i>			17.8	(164 ± 78) nm and (25 ± 5) μm
<i>C</i>	<i>O</i>	<i>Fe</i>													
<i>atom %</i>	<i>atom %</i>	<i>atom %</i>													
57.20	21.72	21.06													
<i>O/C = 0.38, Fe/C = 0.37, Fe/O = 0.97</i>															
Ex-PN@Dr-ZVI	<table> <tr> <td><i>C</i></td> <td><i>O</i></td> <td><i>Fe</i></td> </tr> <tr> <td><i>atom %</i></td> <td><i>atom %</i></td> <td><i>atom %</i></td> </tr> <tr> <td>52.25</td> <td>20.76</td> <td>26.98</td> </tr> <tr> <td colspan="3"><i>O/C = 0.40, Fe/C = 0.52, Fe/O = 1.30</i></td> </tr> </table>	<i>C</i>	<i>O</i>	<i>Fe</i>	<i>atom %</i>	<i>atom %</i>	<i>atom %</i>	52.25	20.76	26.98	<i>O/C = 0.40, Fe/C = 0.52, Fe/O = 1.30</i>			24.7	(194 ± 69) nm and (25 ± 5) μm
<i>C</i>	<i>O</i>	<i>Fe</i>													
<i>atom %</i>	<i>atom %</i>	<i>atom %</i>													
52.25	20.76	26.98													
<i>O/C = 0.40, Fe/C = 0.52, Fe/O = 1.30</i>															

*Atoms peak regions: Carbon (C, 0.278 keV), Oxygen (O, 0.550 keV) and Iron (0.725 keV and 6.432 keV)

** Weight % of immobilized iron availed from TGA analysis.

X-ray diffraction (XRD) analysis

In order to determine the precise nature of iron particles immobilized in the nonwovens, all prepared samples were characterized by XRD. An example of the XRD spectrum of the nanoscale iron particles is shown in figure 8. Apparent peaks at the 2θ of 44.9° and 35.8° indicate the presence of both zero-valent iron (α -Fe) and iron oxide (Fe_2O_3 and Fe_3O_4) crystalline phases [28, 77]. As seen, broad peaks at 44.9° were displayed for all nonwoven with immobilized iron particles. This feature peaks suggest that the surface of iron nanoparticles consist mainly of a layer of iron oxides, likely in the form of iron oxides as illustrated in scheme 3. These results are in general consistent with reported work suggesting a core-shell structure for the iron nanoparticles.

Figure 8: Determination of precise nature of iron particles immobilized in the nonwovens through XRD analysis; (a) PN, (b) In-PN-ZVI, (c) Ex-PN-ZVI, (d) In-PN@Dr-ZVI and (e) Ex-PN@Dr-ZVI.

3.3. Discussion on stabilization and immobilization of zerovalent iron

Plasma treatment of the PET fiber surface creates both carboxylic (-COOH) and hydroxyl (-OH) terminal groups on the fiber surface. All hydrophilic groups are exposed to ferric ions binding them first, and there is subsequent reduction of the bound free ferric ions by the sodium borohydride, producing immobilized ZVI. Size-distribution and coloration of iron particles immobilized on the nonwoven seem to depend on the method of iron reduction (in-situ or ex-situ) used and on the type of PET surface activation used (plasma with/without dendrimer grafting). On plasma treated samples without dendrimer, overall coverage of fiber surface with nano to sub-micronic size iron particles (50 to 700 nm), was observed turning from black to yellowish brown color almost immediately. More uniform and finer deposits of nanoparticles was achieved for in-situ method compared to thicker and irregular deposits for the ex-situ method. On dendrimer grafting of plasma treated nonwovens, black micro particles (25 μm) inside the fiber nonwoven webs are observed, in addition to nanoparticles on the fiber surface. These nanoparticles turned to yellowish brown in the in-situ method, and stayed black in the ex-situ method. Presence of yellowish iron particles present on the plasma treated PET nonwoven (see Figure 4) would be explained by the formation of an outside iron oxide core layer on the zero valent iron particles [14, 78] as illustrated in scheme 3. In aqueous solution, as a result of surface hydroxylation, the surface is likely in the form of FeOOH [40, 77].

However, oxide shells have been shown to reduce the risk of further oxidation of ZVI and provide a degree of stabilization of zero valent iron particles [14]. Oxide layer in ZVI immobilized PET nonwoven observed in optical microscope and XRD analysis, provides evidence of successful stabilization of nano to sub-micronic zero valent iron particles. Blackish micro/nano iron particles in dendrimer grafted nonwovens manifest the effectiveness of dendrimers for the stabilization of zero valent iron.

Scheme 3: Schematic illustration of iron oxide shell formation

PART 2- Analysis of Fenton-like degradation of water pollutant

3.4. Heterogeneous Fenton-like degradation of malachite green using ZVI immobilized PET nonwoven

Degradation of malachite green dye

To investigate the potential environmental applications of ZVI immobilized PET nonwovens, these were used as catalyst for heterogeneous Fenton-like degradation of malachite green dye in aqueous solution. Fenton-like reaction involves the combined use of ferrous ions and hydrogen peroxide (H_2O_2) to produce highly oxidation potential active oxygen species capable of degrading organic contaminants. Malachite green is a common basic organic dye-containing aromatic ring, which is resistant to traditional chemical and biological removal methods [79]. Using the conditions described in section 2.4.5, the UV/visible spectroscopic analysis was used to study color removal of malachite green in presence of ZVI immobilized PET nonwovens (see Figure 9). The characteristic absorption peak of malachite green at $\lambda_{620\text{ nm}}$ significantly decreased within 20 to 70 min depending on the type of immobilized ZVI nonwoven used. The kinetics of malachite green color removal is summarized in table 4.

ZVI as reported in many literature work [14, 18, 78, 80, 81], have been shown to exhibit catalytic properties. Here ZVI immobilized on nonwovens showed good color removal efficiency. No visible color removal was observed in control experiments performed using nonwovens without ZVI, i.e. the dendrimer grafted PET nonwoven or plasma treated PET nonwovens alone (see Figure S2 in supplementary information). ZVI immobilized on dendrimer grafted PET nonwoven using ex-situ reduction- Ex-PN@Dr-ZVI showed the fastest degradation of malachite green dye where 98% color removal was achieved within 20 min, at constant rate of 0.1534 min^{-1} , with a correlation coefficient of the linear regression of about 0.9804. Comparatively, slower rate constant observed with the other ZVI immobilized nonwovens, can be due to the participation of lower amount of ZVI in $\bullet\text{OH}$ radical production. Indeed, the rate of color removal seems to be correlated to the % weight of iron immobilized on each nonwoven as discussed in section 3.2.2 (also see Table 3).

Figure 9: UV-visible spectroscopy of Fenton-like degradation MG ($\lambda_{620\text{nm}}$) using ZVI immobilized nonwoven In-PN@-ZVI (a), Ex-PN@-ZVI (b), In-PN@Dr-ZVI (c), and Ex-PN@Dr-ZVI (d). Conditions: MG = 20 mg/L, ZVI immobilized nonwoven = 1 cm², H₂O₂ = (0.5 mL, 0.3 M).

Kinetics of degradation of malachite green dye

The [instant /initial] absorbance ratio of the malachite green band at $\lambda_{620\text{ nm}}$ (A_t/A_0), which accounts for the corresponding concentration ratio (C_t/C_0), allows plotting of $\ln(C_t/C_0)$ as a function of time as shown in figure 10b-c. Model validation of the Pseudo-first-order kinetics for MG color removal with the catalyst is obtained by the linear evolution in time of $\ln(C/C_0)$, more particularly for ZVI immobilized PET nonwoven samples, as supported by R^2 values beyond 0.98 (see Table 4). Plots summarized in table 4 shows that all ZVI immobilized nonwoven samples exhibited good linear relationships of $\ln(C_t/C_0)$ versus reaction time following pseudo-first-order kinetics with respect to malachite green color removal. These results are consistent with those found in previous reports [14, 33, 82, 83].

Fig. 10: Evolution of the C_t/C_0 (a) and $\ln(C_t/C_0)$ (b) degradation and conversion (c) as a function of time at room temperature of MG. Conditions: MG = 20 mg/L, ZVI immobilized nonwoven = 1 cm², H₂O₂ = (0.5 mL, 0.3 M).

Table 4: Pseudo-first-order kinetics study for the Fenton-like degradation of malachite green $(\lambda_{620 \text{ nm}})$.

ZVI immobilized nonwovens	Time (min)	MG degradation	
		* $k(\text{min}^{-1})$	** R^2
<i>In-PN-ZVI</i>	70	0.0469	0.9506
<i>Ex-PN-ZVI</i>	60	0.0645	0.9686
<i>In-PN@Dr-ZVI</i>	40	0.0847	0.9731
<i>Ex-PN@Dr-ZVI</i>	20	0.1534	0.9824

* k is the rate constant per 1 cm^2 catalyst for the pseudo-first-order kinetics and is expressed in min^{-1}

** R^2 is the correlation coefficient of the linear regression.

As shown in table 4 and figure 10, the Ex-PN@Dr-ZVI shows a considerably high catalytic efficiency considering time, rate constant per unit size of heterogeneous catalysts and % of color removal of malachite green due to Fenton-like degradation, as discussed already. However, the color removal rate using In-PN-ZVI, Ex-PN-ZVI and In-PN@Dr-ZVI nonwovens reaches 95% in 70 min., 97. % in 60 min., and 97% in 40 min., respectively. Such a high conversion and rapid kinetics in catalytic degradation for color removal might be attributed to the good stability and immobilization of zero valent iron particles ensuring the maximum coverage of active radicals for dye degradation as supported by higher “ k ” values. When compared to numerous catalyst materials reported in the literature for degradation of malachite green (Table 5),

Table 5: A comparison of the degradation of malachite green by Fenton-like treatment.

Catalyst	Conc. of pollutant	Time (min)	Rate constant of color removal k (min ⁻¹)	correlation coefficient, R ²	Number of reusability cycles	Toxicity Reduction in % (TOC/COD)	References
Kssiris/TiO ₂ /Fe ₃ O ₄ /GOx	20 mg/L	120	0.0180	0.990	4	-	[13]
Bio-Fenton	05 mg/L	120	-	-	-	-	[19]
Solar/H ₂ O ₂ /Fe ⁰ -AC	3.5 µM	60	0.0900	0.953	6	-	[22]
OT-Fe-NP/H ₂ O ₂	50 mg/L	60	0.0450	0.980	-	-	[27]
Fe-NP/ H ₂ O ₂	50 mg/L	90	0.0484	0.998	-	70*	[28]
EDTA-Fe(III)/H ₂ O ₂	500µM	60	-	0.990	-	92*	[52]
FeO-Nps/H ₂ O ₂	30mM	240	0.0779	0.9689	6	42*	[32]
In-PN-ZVI/H ₂ O ₂	20 mg/L	70	0.0469	0.950	7	29 4	<i>This Work</i>
Ex-PN-ZVI/H ₂ O ₂	20 mg/L	60	0.0645	0.969	8	60 4	<i>This Work</i>
In-PN@Dr-ZVI/H ₂ O ₂	20 mg/L	40	0.0847	0.973	7	66 4	<i>This Work</i>
Ex-PN@Dr-	20 mg/L	20	0.1534	0.982	8	54 4	<i>This</i>

ZVI/H ₂ O ₂							Work
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*Toxicity reduction percentage in terms of TOC analysis and

↓Toxicity reduction percentage in terms of COD analysis

Recyclability and reusability of the catalyst

One of the greatest issues of the immobilized catalyst on PET nonwoven is the possibility of the catalysts to be recovered and reused in consecutive degradation cycles. In the present work, the reusability of ZVI immobilized PET nonwovens on the heterogeneous degradation processes are reported in figure 11. After each cycle, the catalyst was recovered by simple removal method and prepared for next runs. The results demonstrate that functionalized ZVI immobilized nonwovens catalyst can be recycled and reused more than 07 times maintaining high color removal efficiency, especially in the case ZVI immobilized on dendrimer grafted PET. A confirmation in this regard was obtained from the morphological analysis of the used ZVI immobilized nonwovens after removal of pollutants (see Figure S3 in supplementary information).The presence of considerable amount of iron particles present on the fiber surface of all samples after first use cycle which endorses their potential reusability.

Fig. 11: Catalyst recyclability and reusability analysis towards Fenton-like degradation of malachite green Conditions: MG = 20 mg/L, ZVI immobilized PN = 1 cm², H₂O₂ = (0.5 mL, 0.3 M).

COD and TDS analysis

Color removal implies degradation of the colored dye and its conversion to colorless organic entity, however it does not reflect the complete dye degradation to CO₂ and water, or any reduction in dye toxicity. COD quantifies more precisely the amount of organics in water, and more particularly the oxidizable pollutants found in. Reduction in COD reflects more precisely the degree of degradation of the Malachite green dye.

Thus in this part, the chemical oxygen demand and the total dissolved solids were measured, under controlled temperature and pH. Results for the degradation of malachite green dye solution, subjected to homogeneous Fenton reaction (free ferric ions + hydrogen peroxide) and heterogeneous Fenton reaction using ZVI immobilized PET nonwovens, are summarized in table 6. The whole experimental study was carried out at room temperature. Visual color analysis of untreated malachite green dye solution shows characteristic dark green solution which turns to yellow when the homogeneous Fenton-like degradation is used, whereas heterogeneous Fenton-like degradation using immobilized ZVI nonwoven yields a clear solution of treated water as illustrated in scheme 4. The yellow color which appears after homogeneous Fenton-like degradation can be explained by the formation of yellow colored free iron oxides [18] during radical production which is further supported by high TDS (730 ppm) of treated water. Since TDS values are related to the presence of solid particle in the aqueous solution, the high TDS value would indicate a high level of oxide formation or leaching of immobilized iron particles from nonwovens, during degradation of malachite green. COD reduction is barely seen in the homogeneous catalysis, most probably because there is interference of ferrous ions which can be oxidized by potassium dichromate used for COD tests (see section 2.4.5).

Among ZVI immobilized PET nonwovens treated water, minimum (52 ppm) and maximum (229 ppm) average TDS was recorded for In-PN-ZVI and Ex-PN-ZVI, respectively.

Acidification of the effluent and neutralization after homogeneous Fenton-treatment remains a costly and time consuming drawback. It can be seen from table 6 that, while optimal activity of homogeneous Fenton occurs pH 3, the treated water using heterogeneous Fenton-like degradation with immobilized ZVI nonwovens, reaches pH 5 which is more favorable to achieve discharge standard of pH [14, 80].

Table 6: Characteristics detoxification analysis of treated water after Fenton-like degradation of malachite green.

Pollutant	Catalyst	Color	Average		Average
			TDS (ppm)	pH	COD reduction (%)
<i>Untreated</i>	-	Green	49	7	-
<i>Treated</i>	<i>Homogeneous Fenton</i>	Yellowish	730	3	0
	<i>In-PN-ZVI/H₂O₂</i>	Clear	52	5	29.0
	<i>Ex-PN-ZVI/H₂O₂</i>	Clear	229	5	59.6
	<i>In-PN@Dr-ZVI/H₂O₂</i>	Clear	128	5	66.2
	<i>Ex-PN@Dr-ZVI/H₂O₂</i>	Clear	189	5	54.2

Average COD reduction analysis demonstrates that, immobilized ZVI on dendrimer grafted nonwoven showed a considerable reduction of COD as presented in table 8. In the case of heterogeneous Fenton reaction using ZVI immobilized nonwovens, COD reduction increased from 0% to 29.4%, 54.20%, 59.64% and 66.23% for In-PN-ZVI/H₂O₂, Ex-PN@Dr-ZVI/H₂O₂, Ex-PN-ZVI/H₂O₂ and In-PN@Dr-ZVI/H₂O₂ respectively. The main reason for this

tendency may be due to the efficient degradation of MG as well as lower or no formation of secondary pollutants (iron sludge) during treatment of dye.

In the case of homogeneous free iron, COD reduction is barely seen, most probably because there is interference of ferrous ions which can be oxidized by potassium dichromate used for COD tests (see section 2.4.5).

Scheme 4: Illustration and comparison of the dissolved solids particles on the treated solution.

3.5 Mechanism on color removal and mineralization of malachite green dye

Based on the results, plausible mechanism for malachite green degradation was investigated. The underlying mechanisms of degradation of malachite green in the system of ZVI immobilized PET nonwovens in presence of H_2O_2 were considered. The catalytic degradation of MG was attributed to the synergistic effect of Fenton reaction that takes place in the presence of ZVI and hydrogen peroxide that produced highly reactive $\bullet OH$ radicals that oxidize MG. The postulated mechanism for the Fenton like degradation of malachite green dye is represented in scheme 5.

Scheme 5: Postulated mechanism of the catalytic degradation of MG by ZVI immobilized PET nonwoven.

In the heterogeneous Fenton-like system, the generation cycle of hydroxyl radicals by heterogeneous Fenton-like mechanism and mineralization of malachite green dye is shown in reactions (1–11). According to the reaction (1-4), zero valent iron initiate the reaction and lead to generation of Fe^{2+} which is an integral element for Fenton reaction and $\bullet\text{OH}$ radicals formation [84].

(i) The process of formation of iron(II) species

(ii) The process of producing reactive species

(iii) The process of colour removal of MB

(iv) The process of mineralization

In a second step, reactive species are formed which are responsible for dye degradation, with color removal and mineralization of MG.

For mineralization of the intermediates, a further step takes place where reaction intermediates undergo further oxidation and convert into nontoxic substances (see Reaction 10-11).

4. Conclusions

In summary, this work introduces a facile approach to stabilize and immobilize multi-scale zero valent iron on polyester nonwoven using air atmospheric plasma treatment and dendrimer grafting. Plasma treatment activated the hydrophobic PET surface by introducing hydrophilic groups that facilitated iron immobilization whereas further grafting of hyperbranched dendrimer with terminal hydroxyl groups improved the ZVI particles immobilization and stabilization. The synergistic effect of stabilized and immobilized ZVI enabled immobilized iron species on a textile surface become a promising candidate as a

Fenton-like catalyst for commercial wastewater applications maintaining an outstanding properties as summarized follow:

- (a) Resultant materials showed sufficient mineralization of malachite green dye providing 7 and/or 8 consecutive cycle reusability.
- (b) SEM, EDS, TGA analysis revealed that ex-situ reduction methods combined with dendrimer grafting provided highest grafting of ZVI on PET nonwovens. Higher amount of iron present on the ZVI immobilized nonwovens using the ex-situ method, would be responsible for the faster degradation rate of MG, compared to in-situ reduction and immobilization of ZVI.
- (c) Efficient functionalisation methods yield efficient heterogeneous catalyst with robust grafting and high toxicity reduction.
- (d) Potential suggestion for a significant prospect for removal of different pollutants through the heterogeneous catalytic system without production of secondary pollutant (sludge).

This study concludes novel approaches for immobilization and stabilization of ZVI on PET nonwovens, and provides a foundation for the further rational design and technical background for an efficient Fenton-like removal of pollutants in various environments.

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