Supporting information

Iron-loaded amine/thiol functionalized polyester fibers with high catalytic activities: Comparative study

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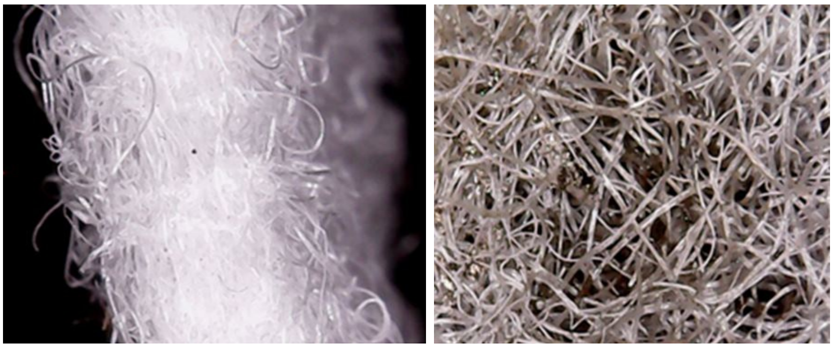
1. Nonwovens characteristics

The PET nonwoven was prepared at the CENT–(Centre Européen des NonTissés) nonwoven prototyping platform (IFTH), using a carding process followed by a spunlacing process using fine water jets under high pressure to consolidate for fiber web consolidation. PET nonwovens surface were cleaned to remove impurities and spinning oil employed during the fabrication steps. Afterwards, the obtained samples were a 100% PET nonwoven, with cylindrical fibers of diameter (**Table 1**).



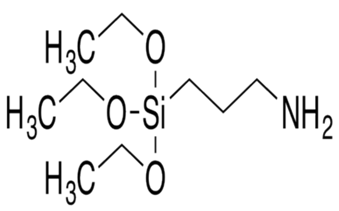
(a) (b)

Fig S1. PET nonwoven catalyst, (a) untreated PET, (b) PET-SH-Fe

Table S1. Characteristics of PET nonwovens

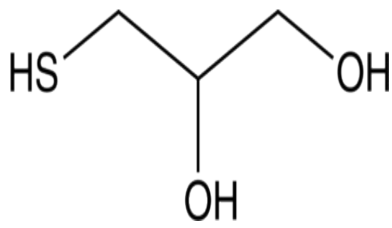
Sample/characteristics	PET
Mass per unit area (g/m^2)	98.00
Thicknesses (mm)	0.94
Fiber density	0.80
Porosity (%)	99.91
Air permeability (mm/s)	854.20

2. Amines and thiol grafted PET nonwovens



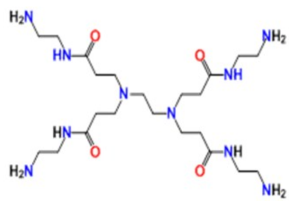
3-(aminopropyl)triethoxysilane

(APTES)



Thioglycerol

(SH)



Dendrimers PAMAM $(NH_2)_4$

(PAMAN)

Table S2. Molecular structure s of the organic moieties grafted.

3. Adsorption isotherms

The Langmuir model is based on the supposition of a homogeneous adsorbent surface with identical adsorption sites [1]. The Freundlich model is an empirical equation which is based on the assumption that there are heterogeneous adsorptions on the surface of the catalyst [1]. In this work, both Langmuir and Freundlich isotherm models were used to analyze the adsorption equilibrium data. The linear form of these two models is given by eqns. 1 and 2 for Langmuir and Freundlich, respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{max}} \qquad (1)$$

$$\text{Ln } q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (2)$$

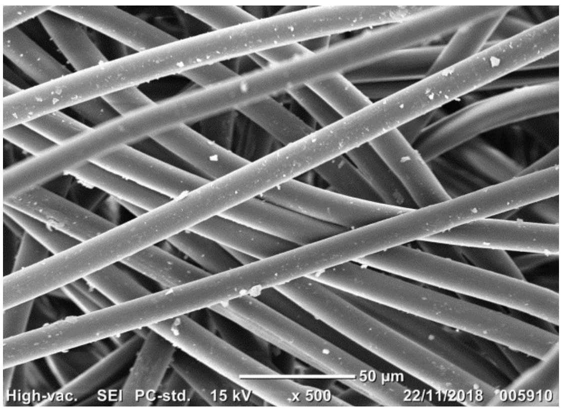
where, q_e is the amount of an adsorbate adsorbed at equilibrium (mg/g), q_{max} the maximum adsorption capacity (mg/g), C_e is the concentration of the adsorbate at equilibrium (mg/L). K_L is the Langmuir constant. K_F is the Freundlich constant in relation to the adsorption capacity. $\frac{1}{n}$ is another constant in the Freundlich model related to adsorption. If the value of $\frac{1}{n}$ is between 0 and 1, this indicates that the adsorption is favourable 34. The Langmuir equation can be the dimensionless factor, RL which is given by eqn. 3 [2].

$$R_L = \frac{1}{1 + K_L C_0} \qquad (3)$$

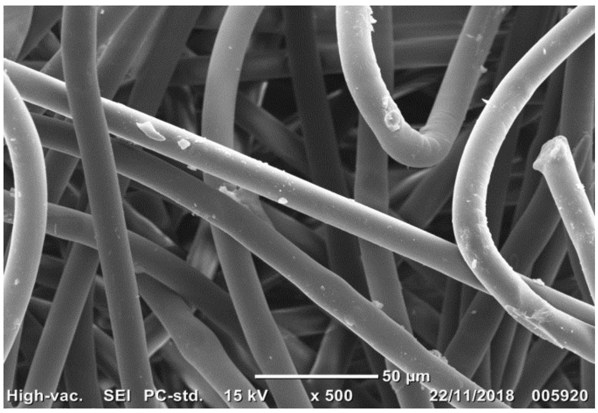
where, K_L is the Langmuir constant and is the highest initial concentration of the adsorbate. The R_L value implies that the adsorption to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

4. SEM analysis

(a)



(b)



(c)

(d)

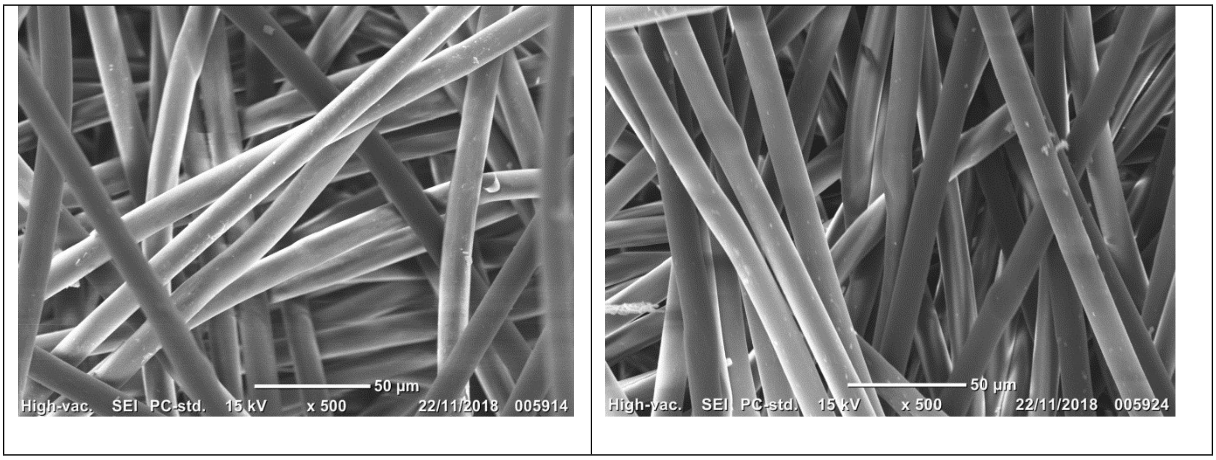


Fig. S2. SEM images of a) PET, b) PET-APTES, c) PET-PAMAN and d) PET-SH samples.

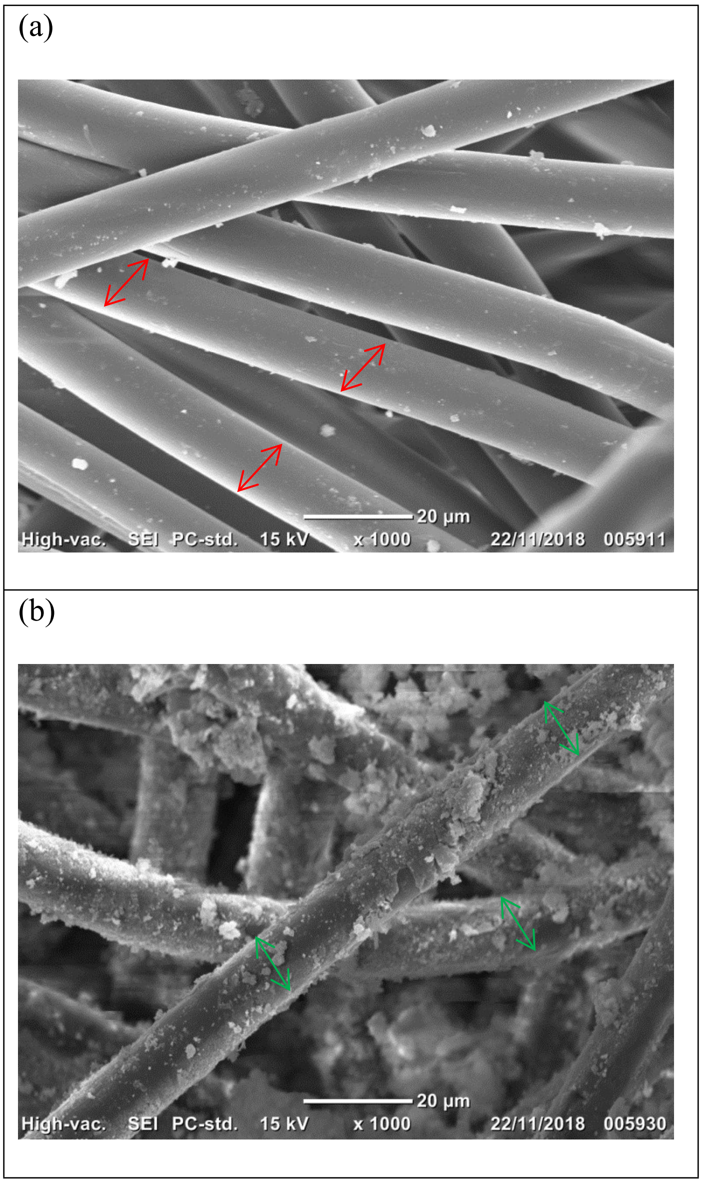


Fig. S3. Changes in the fiber diameter before (a) and (b) after functionalization of PET (a: PET-SH and b:PET-SH-Fe).

5. Optical microscopy analysis

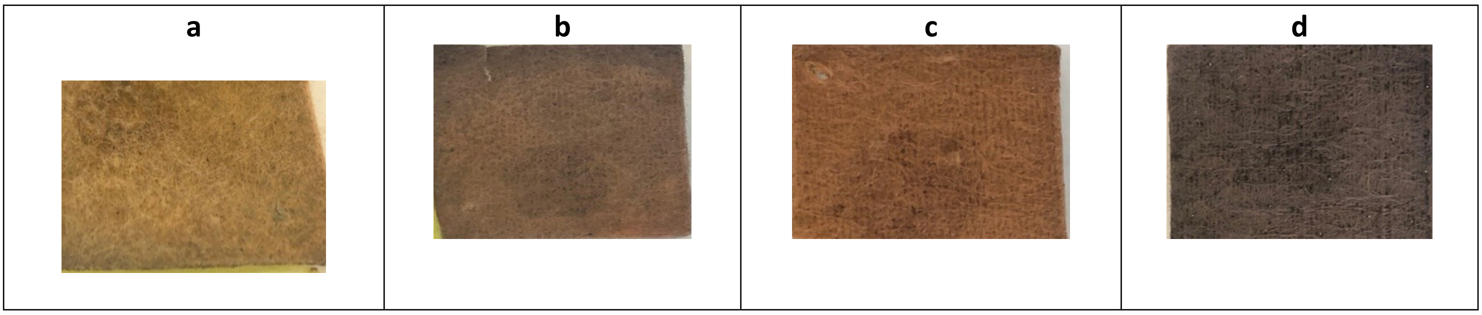
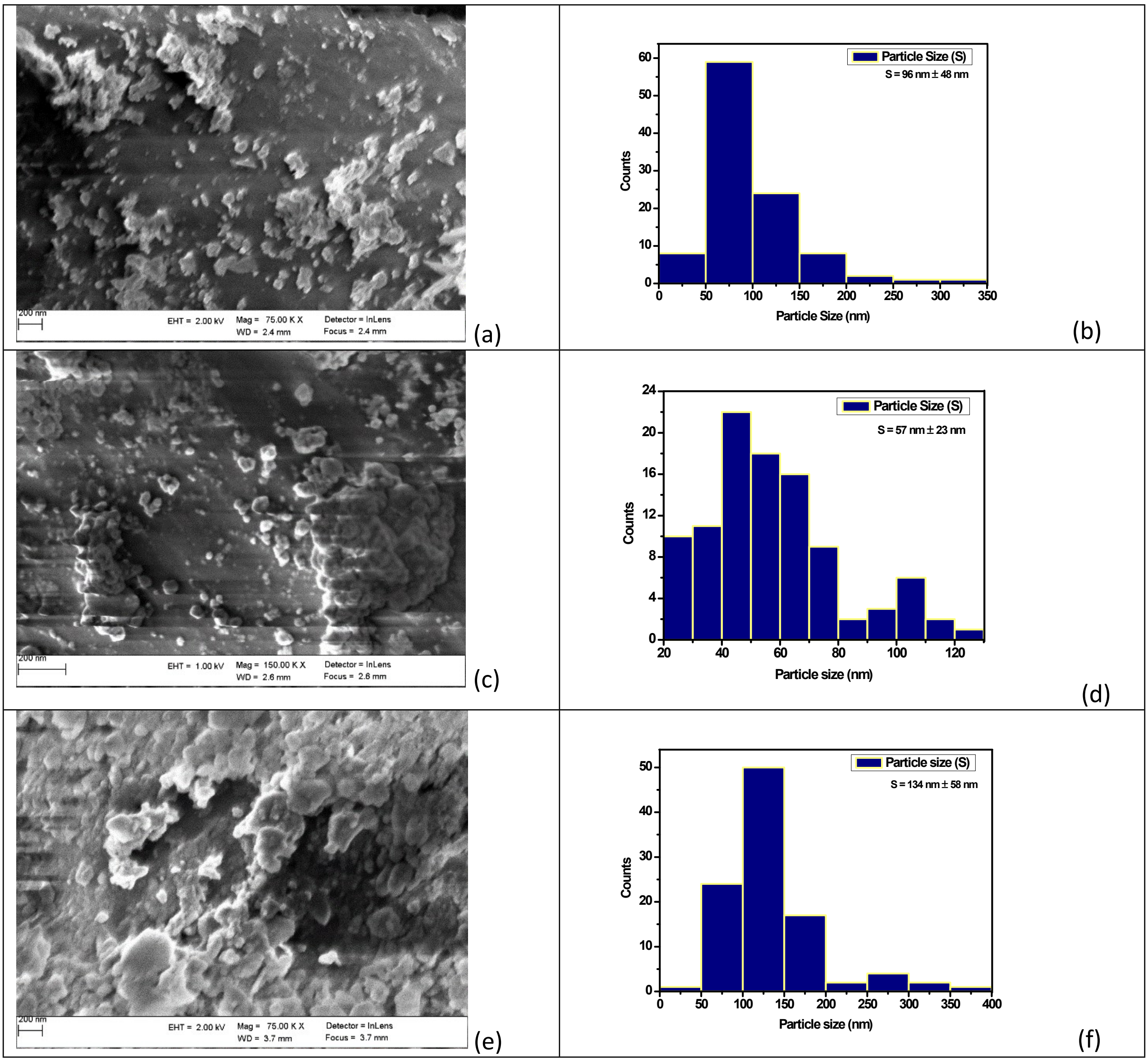


Fig. S4. Photography of a) PET-Fe, b) PET-APTES-Fe, c) PET-PAMAN-Fe and d) PET-SH-Fe samples.

6. Particle size assessment



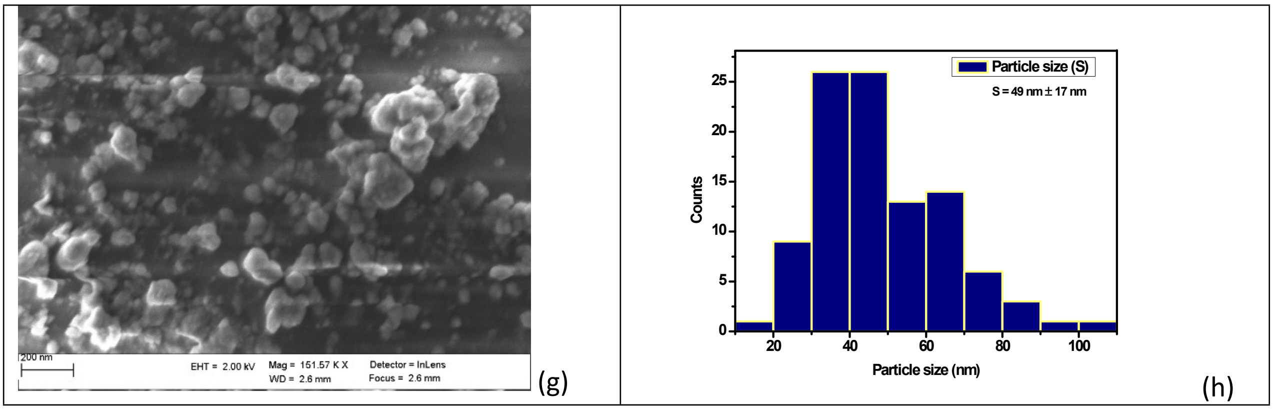


Fig. S4. HR-SEM images and particle size distribution histogram of PET-Fe (a, b), PET-APTES-Fe (c, d), PET-PAMAM-Fe (e, f) and PET-SH-Fe (g, h)

7. FT-IR analysis

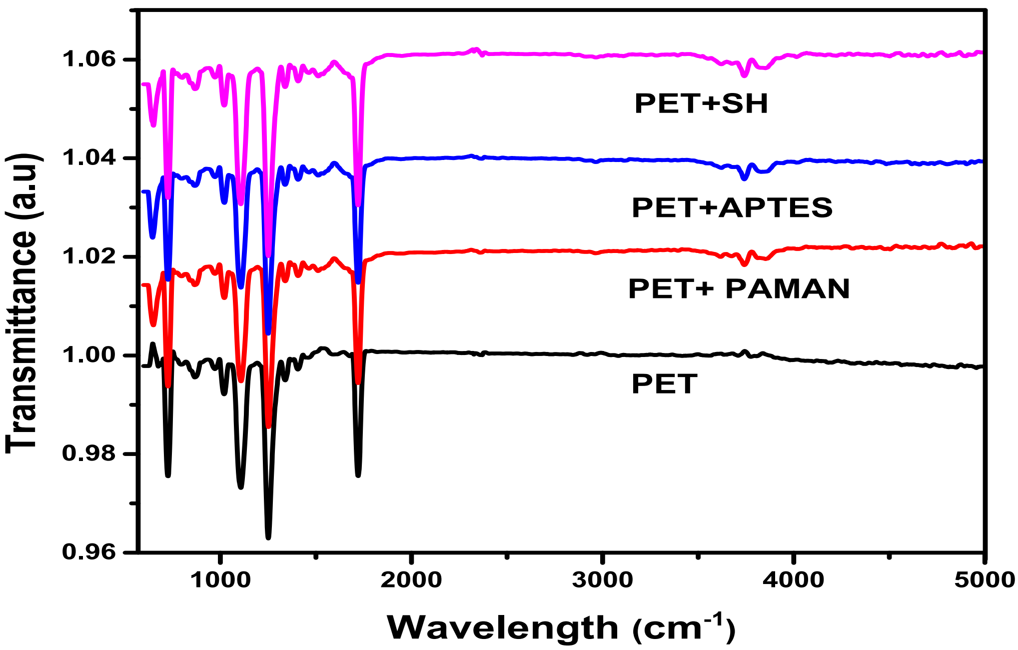


Fig. S5. FTIR spectra of PET, PET-APTES, PET-PAMAN and PET-SH samples.

8. TGA analysis

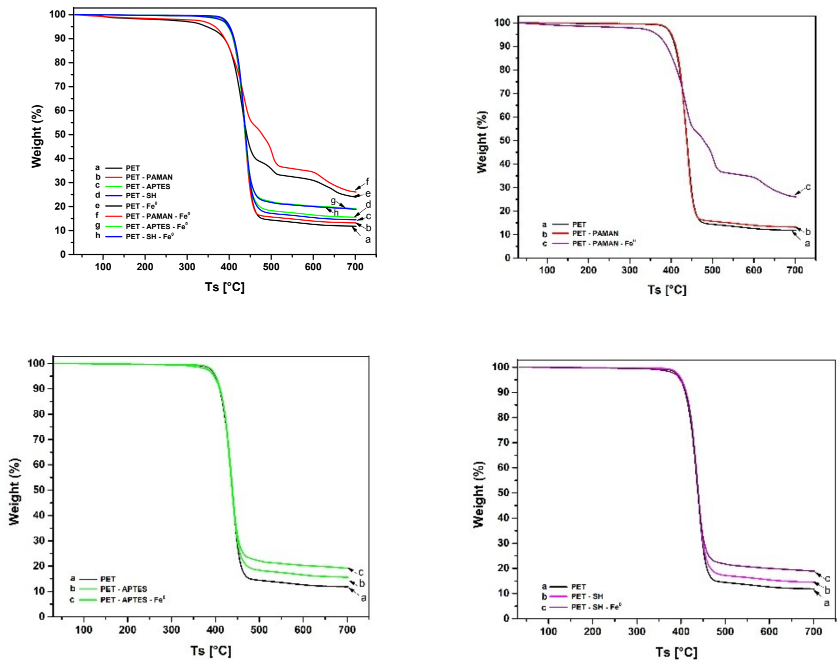


Fig. S6. TGA analysis of treated and untreated nonwovens.

9. DSC analysis

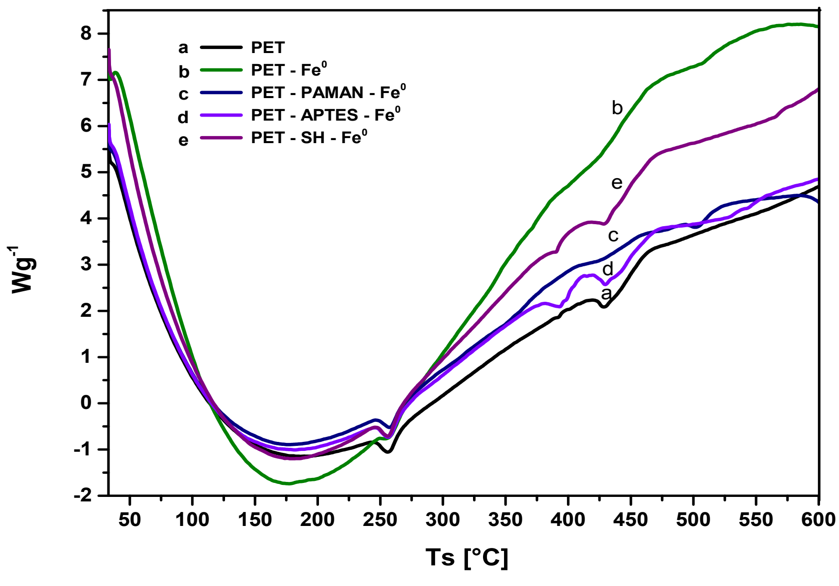


Fig. S7. DSC analysis of treated and untreated nonwovens.

10. Catalytic activity

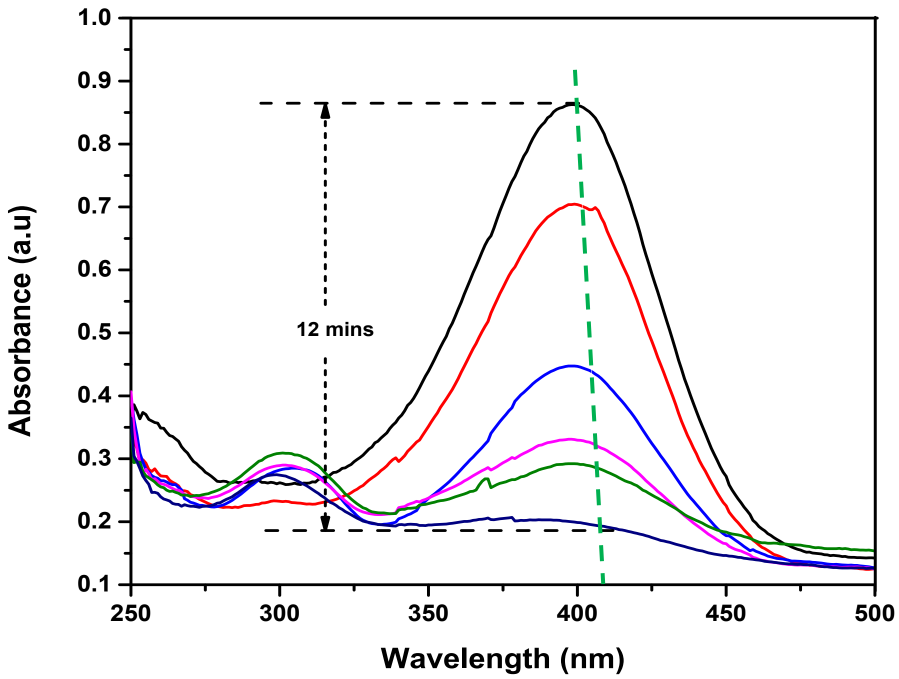


Fig. S8. Shift of the UV-Vis bands towards the low wavelength for 4-NP reduction

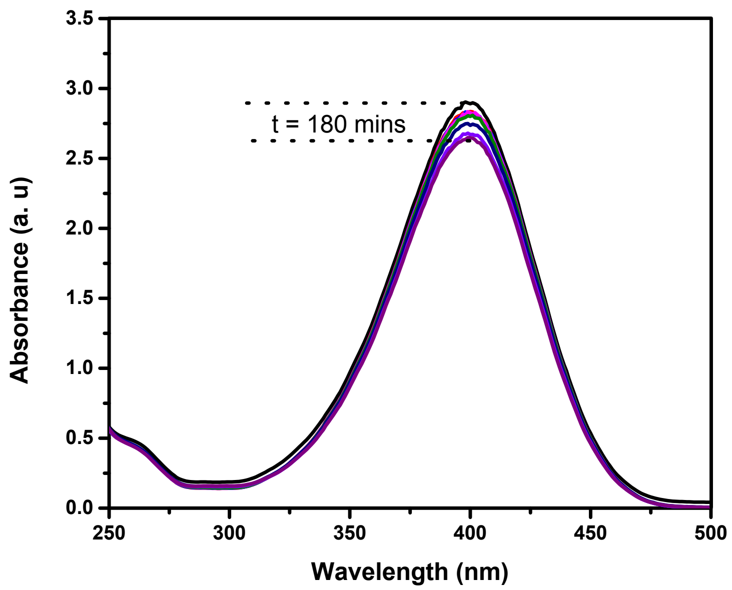


Fig. S9. UV-Vis spectra of 4-NP when contacted with PET-Fe catalyst without reducing agent

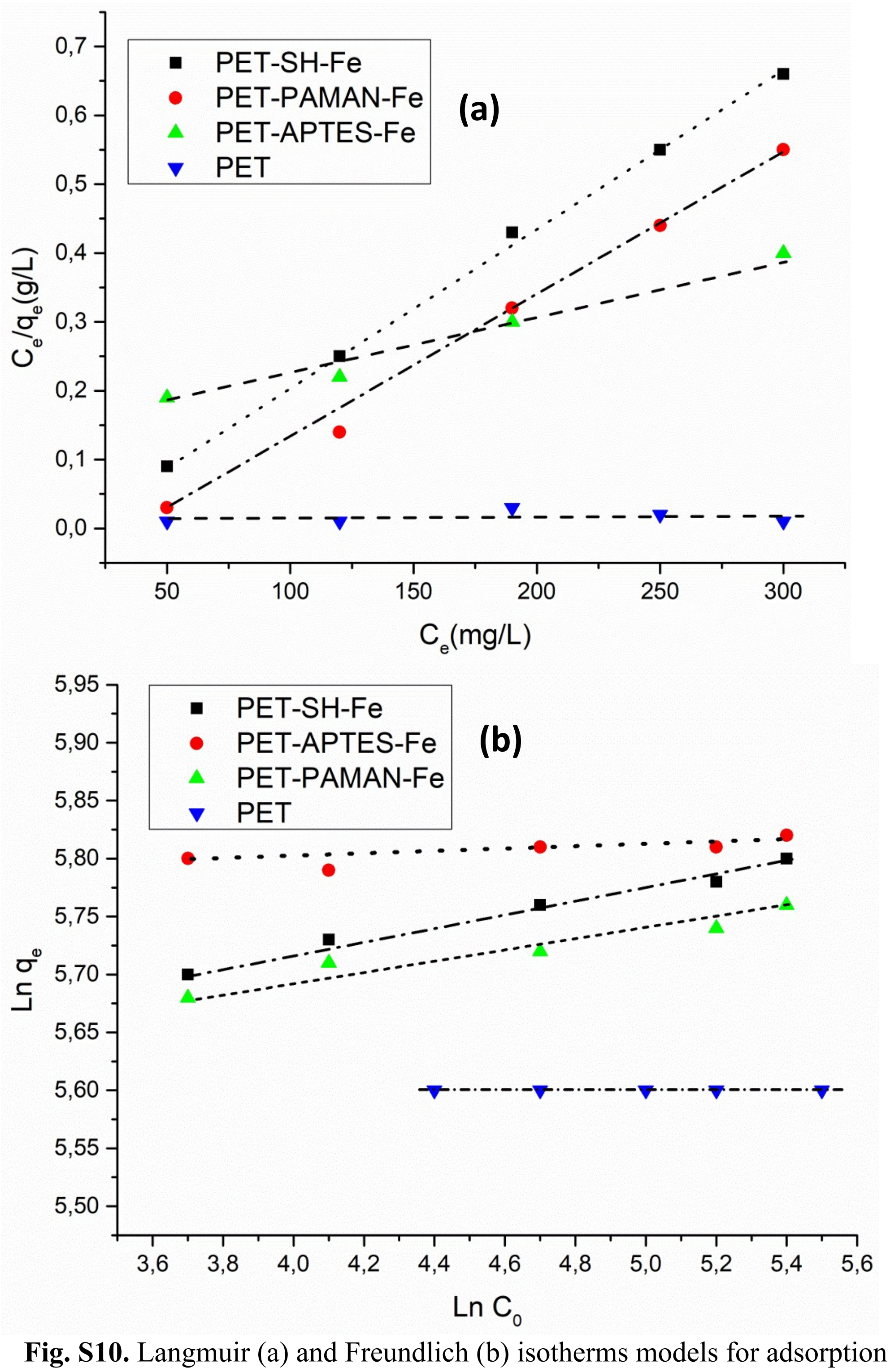


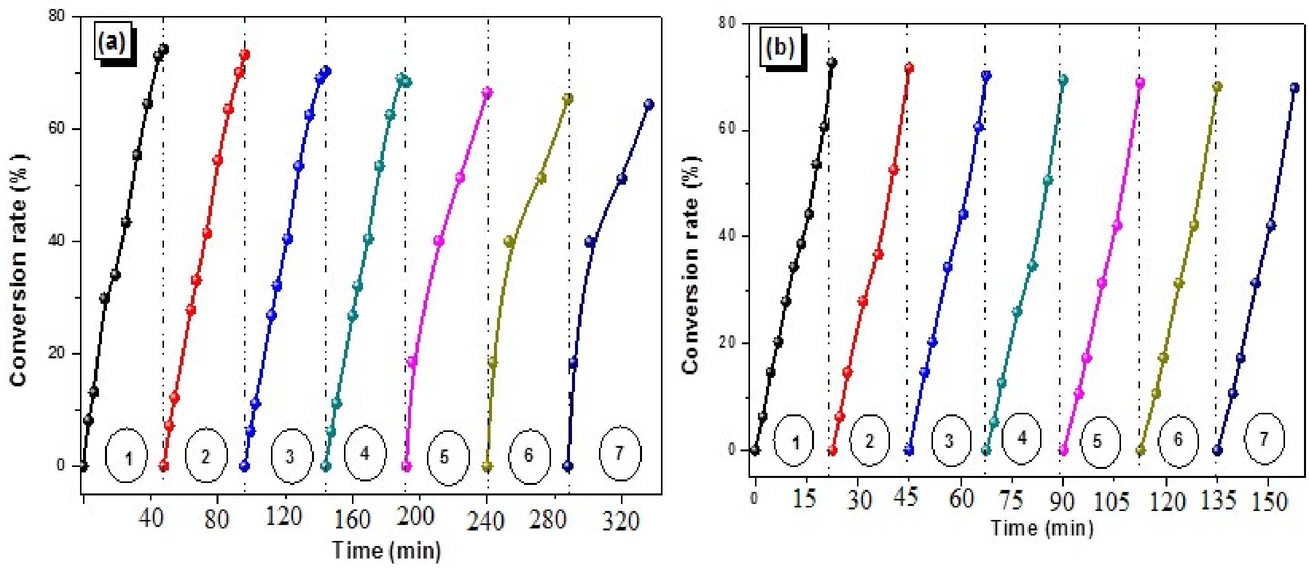
Fig. S10. Langmuir (a) and Freundlich (b) isotherms models for adsorption of 4-NP on the different catalysts

Table S2. Langmuir and Freundlich parameters for 4-NP adsorption on PET-SH, PET-APTES and PET-PAMAN.

Samples	Freundlich isotherm			Langmuir isotherm		
	KF (mg/g) (L/mg)1/n	1/n	R^2	qmax (mg/g)	KL (L/mg)	R^2
PET	270.30	0.812	--	191.56	0.123	--
PET-SH-Fe	173.77	0.144	0.995	350,60	0.051	0.995
PET-APTES-Fe	186.08	0.541	0.920	293.30	0.061	0.989
PET-PAMAN-Fe	191.82	0.640	0.909	269.91	0.081	0.993

The results indicate that the prepared PET-SH-Fe adsorbent has high adsorption affinity towards 4-nitrophenol than the untreated samples. This is due to the higher percentage of iron nanoparticles immobilized into polyester nonwoven, which is more effective in the adsorption process. This confirms that the adsorption of 4-nitrophenol on all Fe-loaded amine and thiol modified polyester fibers is favorable. It was found that the Langmuir isotherm model fits well with the equilibrium data. The Freundlich model also reveals a good correlation.

11. Reusability of Catalyst in 4-NP degradation



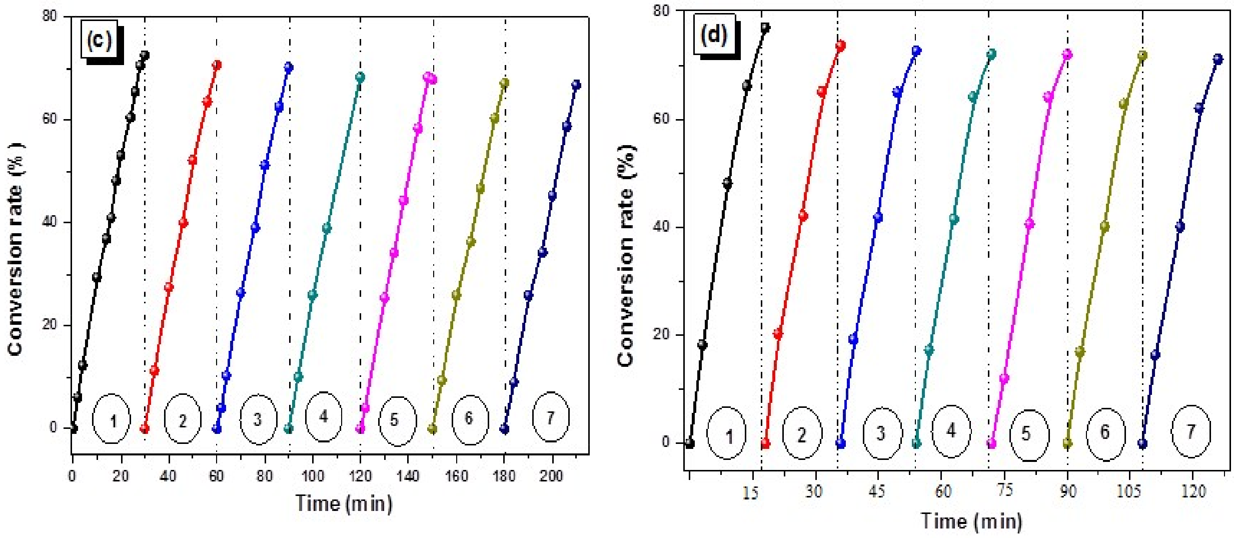


Fig. S11. Catalyst reusability in 4-NP reduction. (a) PET-Fe, (b) PET-APTES-Fe, (c) PET-PAMAN-Fe and (d) PET-SH-Fe catalyst. Reaction conditions: 4-NP=0.5 mM, $NaBH_4$=0.1 M, $m_{catalysts}$=500 mg,T=RT.

Table S3: A comparison of the rate constant for the reduction of pollutants using PET-SH-Fe, PET-APTES-Fe, PET-PAMAN-Fe and other catalysts.

Samples	**Conc. of pollutants**	**Conc. of $NaBH_4$**	**Constant rate (k)**	**Catalyst weight (mg)**	**Time**	**Ref**
	4-Nitrophenol					
Cu_2O@CM	0.09 mM	0.05 M	2.21×10-2 s^{-1}	400	6 min	[60]
AgPd/rGO	0.7 mM	0.5 M	3.65×10-2 s^{-1}	320	3 min	[61]
Fe_3O_4/SiO_2@PDA/Pd	3 mM	0.3 M	1.03×10^{-2}	500	2 min	[62]
Co_3O_4/SBA-15	0.1 mM	0.25 M	--	250	9 min	[63]
$Ag/gC_3N_4/V_2O_5$	0.01 M	0.5 M	0.373 min^{-1}	350	60 min	[64]
CF@CuO-Si-N $(OH)_2$	0.1 M	0.1mM	0.401 min^{-1}	200	10 min	[65]
PF@CuO–Si–$N(OH)_2$	0.1mM	0.1mM	0.401 min^{-1}	200	50 min	[66]
PET_2-APTES-Ag/Cu	0.5 mM	0.1mM	0.177 min^{-1}	*200*	*6* min	[67]
PET-SH-Fe	0.1mM	0.1mM	6.594×10^{-2}	200	12 min	**This work**
PET-APTES-Fe	0.1mM	0.1mM	4.580×10^{-2}	200	15 min	**This work**
PET-PAMAM-Fe	0.1mM	0.1mM	2.437×10^{-2}	200	30 min	**This work**
Samples		**Methylene Blue**				
Ag/Fe_3O_4/RGO	0.06 mM	--	0.007s^{-1}	200	35s	[68]
ZBD@Ag	1 mM	16.6mM	0.0061 s^{-1}	450	6 min	[69]
PC-CuO-DEA	1 mM	0.1mM	0.369min^{-1}	300	8 min	[70]
POA.CA/wool	0.1 M	0.15mM	-	500	45min	[71]
PET-APTES-Fe	0.1mM	0.1mM	3.994×10^{-2}	200	22 min	**This work**
PET-PAMAM-Fe	0.1mM	0.1mM	3.000×10^{-2}	200	30 min	**This work**
PET-SH-Fe	0.1mM	0.1mM	5.487×10^{-2}	200	16 min	**This work**

References

[1]. X. Liu and N.G. Pinto, Carbon, 35, 1387 (1997).
[2]. T. W. Webi and R.K. Chakravort, AIChE J., 20, 228 (1974).