

Tuning the Magnetism of Plasma-Synthesized Iron Nitride Nanoparticles: Application in Pervaporative Membranes

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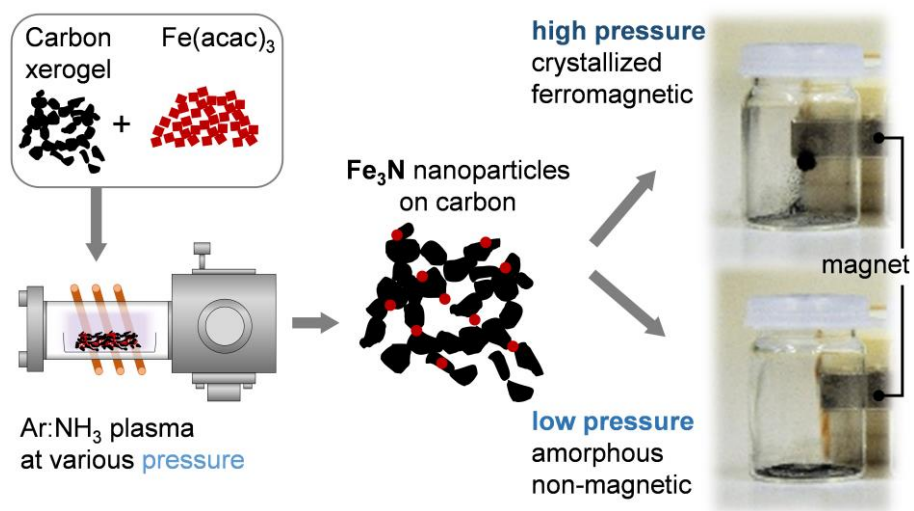
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TOC



ABSTRACT

The present work reports on the low-pressure RF plasma driven synthesis of ϵ -Fe₃N type nanoparticles homogeneously deposited on high surface area porous carbon support, with tuneable magnetic properties, directly depending on the plasma treatment conditions. Iron nanoparticles are formed from the degradation of a solid organometallic precursor mixed with a carbon xerogel in a nitrogen-containing (argon/ammonia) plasma discharge. The variation of the working pressure during the plasma treatment directly affects the residence time of the reactive species, which determines the crystalline state of the nanoparticles, from amorphous at low-pressure to well crystallized at high pressure treatment. It results in a direct influence of the magnetic properties of the iron nitride nanoparticles. The working pressure results in two competing effects as it enhances the crystallinity (at higher pressure) and also slightly affects the surface chemistry of the nanoparticles by increasing the oxygen content; while the last is believed to deteriorate the magnetic properties, however the crystallinity enhancement dominates.

The synthesized Fe_xN/C_{XG} magnetic composites have been applied as filler material in alginate membranes for the ethanol dehydration in a pervaporation experiment. Results indicate a considerably enhanced performance of the alginate membrane as determined by its selectivity, the separation index and the flux even when using a small Fe_xN/C_{XG} loading (3%w/w).

INTRODUCTION

Due to their versatility of chemistry, magnetic properties and crystallinity^{1–3}, the iron nitrides nanoparticles are widely used as catalysts,^{4–7} battery materials,^{8,9} and in medical applications.¹⁰ The low cost and the wide physico-chemical forms of Fe-N compounds bring many advantages compared to noble metal nanoparticles, such as gold or platinum, for the aforementioned applications. The Fe-N system presents numerous different phases, with ferromagnetic compounds such as γ' -Fe₄N, α'' -Fe₁₆N₂ or ϵ -Fe₃N, while FeN is paramagnetic.

Most of the conventional synthesis routes of Fe_xN nanoparticles are liquid-based processes involving multiple reduction, filtration and purification steps, as well as extensive use of solvents, time and energy.^{9,11} Low-pressure plasma treatments offer a valuable and sustainable alternative processing methodology based on the dry synthesis (solvent-free), allowing for the modification of materials by varying the composition of the plasma atmosphere (*i.e.* by injecting inert or reactive species) and by using different solid precursors.^{12,3,13–18} Recently, a plasma-based process was developed to synthesize metal nanoparticles on various high surface carbon substrates (graphene, carbon xerogel, carbon black). The methodology consists in the plasma-induced degradation of a solid organometallic precursor mixed with the carbon substrate resulting in the formation of metal nanoparticles anchored to the carbon matrix.^{19–21}

In this work, we describe the synthesis of magnetic iron nitrides nanoparticles (ϵ -Fe₃N_x) deposited on a carbon xerogel (C_{xG}) through the plasma-induced degradation of iron acetylacetonate in a nitrogen-based plasma discharge (Ar/NH₃). The plasma environment is a complex medium comprising electrons, reactive ionized species, radicals, and neutrals species in non-thermal equilibrium; the working pressure is an easily-accessible variable which allows modifying the plasma intensity (electron density, collision rate) and the residence time of the reactive species. The results show that the organometallic precursor is degraded through multiple reactions with the reactive species in the plasma, progressively leading to the growth of Fe_xN nanoparticles. Additionally, the Fe_xN nucleation,

growth of the crystalline domains and, to a lesser extent, their chemistry, are found to be directly affected by the total working pressure during the plasma synthesis; this variable is thus chosen to easily control and tune the magnetic properties of the Fe_xN nanoparticles.

EXPERIMENTAL

Plasma synthesis of $\text{Fe}_3\text{N}/\text{C}_{\text{XG}}$ samples

A total mass of 30 mg, containing carbon xerogel (C_{XG}) and iron acetylacetonate ($\text{Fe}(\text{acac})_3$, Acros Organics, 99%) to reach a total metal loading of 10 wt.%, was introduced in a Petri dish ($\varnothing$ 30 mm), and treated in a radio frequency inductively coupled plasma (ICP-RF) reactor working at 13.56 MHz and 200 W for 1 h. The homogeneous plasma zone is confined in the quartz tube ($\varnothing$ 150 mm), on a length of $\approx$ 20-30 cm, sufficiently larger than the sample size. Prior to the treatment, the chamber was pumped down below 5×10^{-5} Torr (6.6×10^{-3} Pa) by a turbomolecular pump. Argon and ammonia were flown at 5 and 4 sccm respectively, and the total pressure was adjusted using a throttle valve. The carbon and precursor mixture was treated at four different pressures, namely 6, 12, 25 and 45 mTorr (0.8, 1.6, 3.3 and 6 Pa). The **Figure 1** summarized the plasma synthesis.

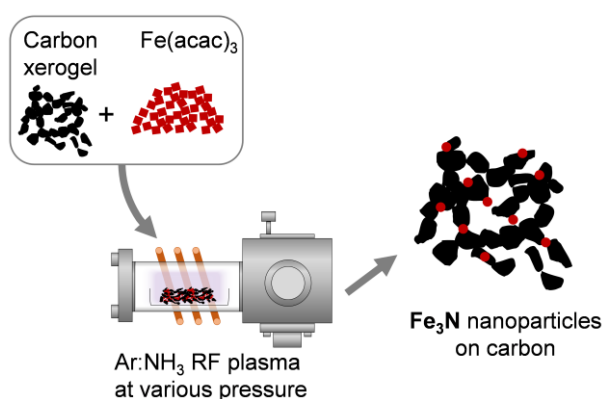


Figure 1. Sketch summarizing the plasma synthesis process of the Fe_3N nanoparticles on xerogel substrate.

Materials characterization

Powder X-ray diffraction (XRD) measurements were performed in an X'Pert Pro Panalytical diffractometer working with the Cu K α 1.5406 Å radiation. The surface composition of the sample was investigated by high-resolution *X-ray photoelectron spectroscopy* (XPS) using a monochromatic Al K α source (K-Alpha instrument from Thermo Scientific). High-resolution spectra were acquired at the pass energy of 30 eV, 0.1eV/step, with numbers of scans adjusted from 10 to 40 to get similar signal-to-noise ratios. A flood gun was used for charge compensation and the spectra were calibrated to the C1s peak at 284.8 eV binding energy. The spectra were fitted using Thermo Advantage Software, using a smart background (Shirley with the additional constraint that the background should not be of a greater intensity than the actual data at any point in the region). *Magnetometry measurements* were performed on a Quantum Design Physical Property Measurement System (PPMS) equipped with a Vibrating Sample Magnetometer (VSM) option. The powder samples were placed in gelatine capsules inside plastic straw sample holders for magnetic characterization. Hysteresis loops were obtained at 5, 10, 20, 50, 100, 200, and 300 K, with applied magnetic fields up to 9 T. *Transmission electron microscopy* (TEM) investigations were carried out using a JEM - ARM 200F Cold FEG TEM/STEM operating at 200 kV and equipped with a spherical aberration (Cs) probe and image correctors (point resolution 0.12 nm in TEM mode and 0.078 nm in STEM mode). For the analysis, samples were sonicated in cyclohexane and a drop was deposited on a copper grid.

Pervaporation experiment.

The pervaporation setup and theoretical background are provided as supplementary information. The pervaporative experiments were carried out using alginate membranes mixed with the Fe_xN/C_{xG} nanocomposite synthesized at 45 mTorr, *i.e.* the sample showing the highest magnetism. The membrane, with an effective size of 112 cm², was synthesized from a 1.5 wt.% sodium alginate solution made by dissolving an appropriate amount of sodium alginate powder in deionised water. The solution was mixed with the Fe_xN/C_{xG} portion to reach 0, 1, 3, 5 or 10 wt.%. The sodium alginate

solution was then casted onto a levelled glass plate and evaporated to dryness at 40°C. After 24 h, the membrane was cross-linked using calcium chloride. For this, the sodium alginate membrane was immersed in 2.5 wt.% calcium chloride solution for 120 min at room temperature. The pristine alginate membrane was prepared following the same methodology except from the addition of the $\text{Fe}_x\text{N}/\text{C}_{\text{XG}}$. The casting conditions were optimized to end up with homogeneous membranes with a reproducible thickness, which was measured using a waterproof precise coating thickness gauge MG-401 ELMETRON. The thickness estimated from at least 10 measurements at different locations is 22 ± 1 μm . The membrane was placed on a finely porous stainless steel plate support. After ethanol/water separation within the membrane module, the retentate was recirculated to the feed tank and the permeate was received and frozen in the cold trap. The composition of the feed, the permeate and the retentate were analysed by gas chromatography on a PerkinElmer Clarus 500 GC equipped with 30 m elite-WAX ETR column and FID detector.

RESULTS AND DISCUSSIONS

Structural properties analysis

The degradation of the organometallic precursor and the subsequent crystallization of Fe_xN domains by the plasma treatment at various total working pressures between 6 and 45 mTorr were investigated by X-Ray diffraction (XRD) measurements (**Figure 2a**). The working pressure was simply increased by reducing the pumping speed thanks to an intermediate throttle valve. The obtained diffraction peak positions indicate possibly the formation of Fe_2N or Fe_3N trigonal structures (space group 149–P312), or $\epsilon\text{-Fe}_3\text{N}$ hexagonal iron nitride structures (space group 182–P6₃22). Because of the very similar XRD patterns, it is difficult to discriminate between Fe_2N , Fe_3N , $\epsilon\text{-Fe}_3\text{N}$ or other intermediate structures ($\text{Fe}_3\text{N}_{1.1}$, $\text{Fe}_3\text{N}_{1.33}$, ... $\text{Fe}_3\text{N}_{1.5}$).^{22,23} Despite this complication, based on the relative peak intensities and positions, the experimental XRD patterns obtained at various pressure values result in

the best agreement with ϵ -Fe₃N_{1.33} (hexagonal) structure,²³ but a mix of Fe₂N and Fe₃N is not excluded. A deeper investigation on the structure is presented later, based on TEM measurement. The XRD patterns indicate that nanoparticles synthesized at 6 mTorr are almost amorphous, as the diffraction peak are not clearly defined. By increasing the treatment pressure, the main features of the XRD pattern do not change; however one clearly observes the reduction of the full width at half maximum (FWHM) of the (111) diffraction peak (Figure 2b). Based on the Debye-Scherrer formula, the decrease of FWHM can be correlated with the increase of the average crystal domain size from ~10.5 nm (at 12 mTorr) to ~13 nm (at 45 mTorr).

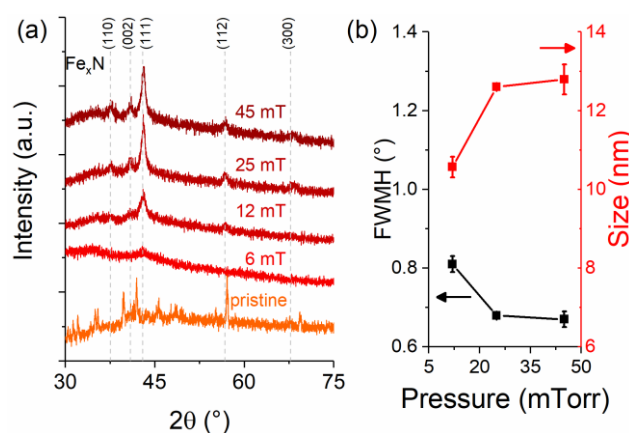


Figure 2. (a) XRD measurements of the untreated powder mixture of the precursors (pristine) and the Fe_xN/C_{XG} composites obtained by Ar:NH₃ plasma treatments at various total working pressures. (b) Variation of the FWHM of the most intense reflection (111) and the derived domain size using the Scherrer formula.

The size distribution of Fe_xN nanoparticles on the carbon xerogel were further investigated by STEM (**Figure 3**). Overall, the micrographs confirm that homogeneously dispersed nanoparticles decorate uniformly the porous carbon surface. In agreement with XRD analysis, the increase of the total working pressure results in increasing the average particle size; however, as frequently reported, the XRD analysis tends to overestimate the domain size, due to the highly weighted particle aggregates. The SAED patterns present very diffuse and unclear rings for nanoparticles at 6 mTorr (Figure 3c),

suggesting amorphous or poorly crystallized nanoparticles. In contrary, at 45mTorr, the reflexion is more intense and more defined (Figure 3d), in accordance with crystallized nanoparticles, with the possibility to index several planes at $d = 0.163, 0.210, 0.221$ and 0.239 nm.

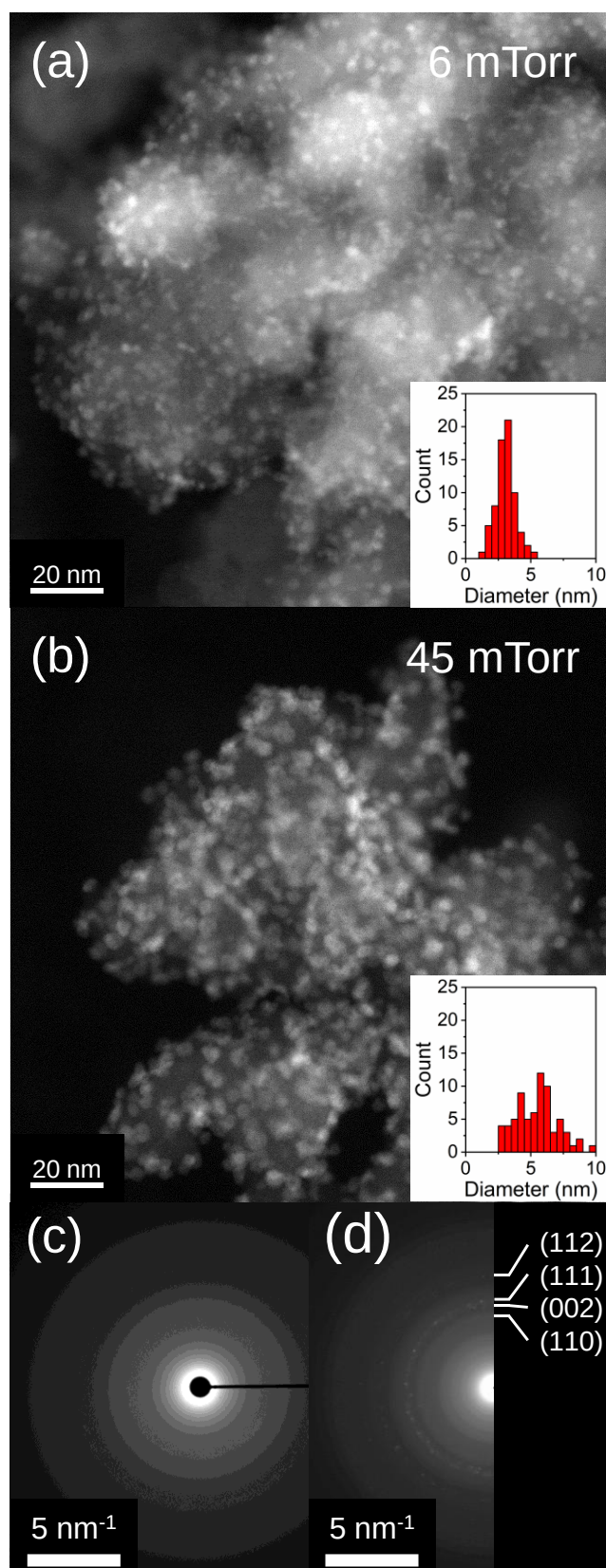


Figure 3. STEM HAADF micrographs of samples treated under (a) 6 mTorr and (b) 45 mTorr, with nanoparticles size distribution in the insets. Selected area electron diffraction patterns of samples treated under (c) 6 mTorr and (d) 45 mTorr.

The experimental values d_{exp} determined on Figure 2d have been compared with reported values d_{theo} for several iron nitride structures. We compared our d_{exp} values with Fe₂N trigonal structure (SG 149, work from Hendricks et al.²⁴), Fe₃N trigonal structure (SG 149, work from Hendricks et al.²⁴ and Jack et al.²²), ϵ -Fe₃N hexagonal structure (SG 182, work from Jacobs et al.²⁵), and ϵ -Fe₃N_{1+x} hexagonal structure (SG 182) with x ranging from 0.1 to 0.39 (work from Leineweber et al.²³). The **Table 1** present the comparison with the relative error δ given in %.

Table 1. Comparison of experimental d values for (112), (111), (002) and (110) planes with several iron nitride structures

		Planes			
		(112)	(111)	(002)	(110)
This work	d_{exp} (nm)	0,162(9)	0,210(1)	0,221(3)	0,239(1)
Ref ²⁴	d_{theo} (nm)	0,1624	0,2106	0,2209	0,2397
Fe ₂ N trigonal (SG 149)	$\delta_{\text{theo/exp}}$ (%)	0.30	0.26	0.20	0.23
Ref ²⁴	d_{theo} (nm)	0,1593	0,2058	0,2181	0,2334
Fe ₃ N trigonal (SG 149)	$\delta_{\text{theo/exp}}$ (%)	2.26	2.09	1.47	2.44
Ref ²²	d_{theo} (nm)	0,1607	0,2078	0,2197	0,2358
Fe ₃ N trigonal (SG 149)	$\delta_{\text{theo/exp}}$ (%)	1.34	1.12	0.73	1.40
Ref ²⁵	d_{theo} (nm)	0,1584	0,2081	0,2161	0,2329
Fe ₃ N hexagonal (SG 182)	$\delta_{\text{theo/exp}}$ (%)	2.82	0.98	2.40	2.65
Ref ²³	d_{theo} (nm)	0,1608	0,2079	0,2197	0,2360
Fe ₃ N _{1.1} hexagonal (SG 182)	$\delta_{\text{theo/exp}}$ (%)	1.30	1.06	0.71	1.32
Ref ²³	d_{theo} (nm)	0,1620	0,2099	0,2208	0,2386
Fe ₃ N _{1.33} hexagonal (SG 182)	$\delta_{\text{theo/exp}}$ (%)	0.56	0.10	0.23	0.21

Considering the uncertainty on the determination of d_{exp} , the lowest differences are obtained with Fe₂N trigonal structure²⁴ and Fe₃N_{1.33} hexagonal structure²³, with similar δ of 0.2-0.3%, while the difference reaches several % for other structures. However, Fe₂N does not present ferromagnetic behaviour,^{26,27} suggesting an indexation in agreement with Fe₃N_{1.33} structure.

Chemical properties analysis

The evolution of the sample chemistry as a function of the plasma synthesis pressure was investigated by EDS measurement (**Table 2**) and XPS chemical analysis of Fe 2p, O 1s and N 1s core level (**Figure 4**). The quantification from XPS analysis is not reliable, since it is a surface composition that can be influenced by the morphology of the sample (nanoparticles size). Even if EDS is generally not recommended for quantification of light elements, a recent work from Woodward et al. suggests that

is can be used to investigate the chemical composition of nanoparticles.¹⁶

In the present work, EDS analysis has only been used for qualitative comparison of the concentration of iron, oxygen and carbon. Nitrogen was not quantified, as its discrimination with oxygen on EDS spectra is challenging in case of low N content. The quantification (**Table 2**) exhibits a similar concentration for samples synthesized at 12, 25 and 45 mTorr. The sample synthesized at 6 mTorr contains a higher oxygen content.

Table 2. Estimated mass concentration of samples from EDS measurements

Pressure (mTorr)	Mass concentration (wt%)		
	Fe	O	C
6	6 ±1	22±1	72±1
12	11±1	16±1	73±2
25	12±2	17±2	71±3
45	14±2	18±1	68±1

In addition to EDS measurements, that give a rough estimation of the global composition of the sample, the XPS high resolution spectra of O 1s, N 1s and Fe 2p have been fitted, giving information on the nanoparticles chemistry. We only present the fits for 6mTorr sample and the relative variation of each contribution as a function of the pressure, but all the fits are given in supplementary information (Figure S-1).

The O 1s spectra (Figure 4a) feature three chemical components, attributed to O-metal (at 529.8 eV), O-C or O-H (at 531.6 eV) and O in H₂O (at 533.6 eV).^{28,29} The Fe 2p doublet spectra (Figure 4b) indicate the presence of Fe⁰ (2p_{3/2} at 707.6 eV), Fe⁺² (711.0 eV) and Fe⁺³ (713.7 eV) chemical states^{28,30}. For simplicity, satellites peaks in the binding energy (BE) range 717-721eV have been fitted with a single component, with the corresponding doublet at $\approx$ 732 eV. The N 1s spectra (Figure 4c) feature three chemical components corresponding to pyridinic nitrogen (at 399.4 eV), pyrrolic nitrogen (at 403.3 eV),^{19,28} and iron nitride/oxynitride (at 396.7 eV).^{29,31} Many XPS studies have been previously devoted to fitting the N 1s spectrum in iron nitride/oxynitrides and other transition metal nitrides to evidence the evolution of the spectrum with the oxygen content: the oxynitride peak (at 396.1 eV) was generally found to shift about 1 eV toward low binding energies (BEs) with respect to the nitride peak

(397.4 eV).^{29,32–35} The reason for this shift was ascribed to the increase of charge transfer from the metal to the nitrogen atom when the oxynitride is formed.³⁴ Here, with the calibration of the C 1s at 284.8 eV, the nitride/oxynitride N 1s component is centered at 396.7 eV (with a FWHM value of 1.4 eV), suggesting a balanced mixture between the two chemical states (nitride and oxynitride). Looking at samples synthesized at various pressure, this nitride/oxynitride contribution, together with the O-metal contribution in the O 1s spectrum, increases when increasing the plasma synthesis pressure (Figure 4d), indicating a potential oxynitridation of the nanoparticles at higher pressure. This trend is associated with an overall reduction of iron (Figure 4e), confirming the higher incorporation of nitrogen (N^{3-} instead of O^{2-}). The large presence of O-metal contribution is due to the oxidation of iron nitride nanoparticles, as frequently reported.^{36–38}

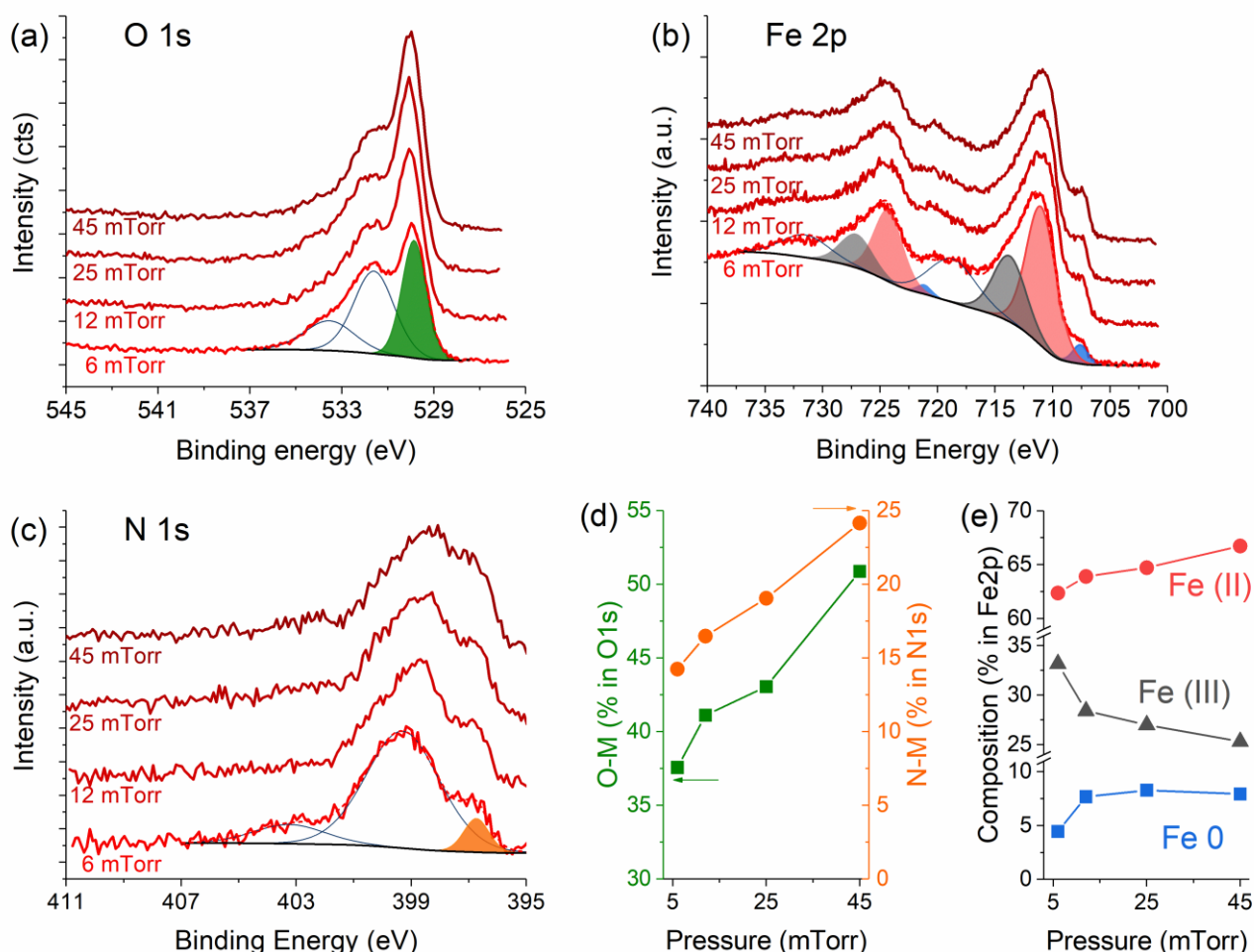


Figure 4. Evolution of the (a) O 1s, (b) Fe 2p, (c) N 1s core level XPS spectra as a function of the total working pressure during the plasma synthesis. (d) Evolution of the O-metal and N-metal percentages within the respective O 1s and N 1s core level spectra. (e) Evolution of the percentage of the three components within Fe 2p peak as a function of the plasma pressure.

Some conclusions based on the chemical analysis can be derived about the precursor degradation mechanism, as well as the nanoparticle nucleation and growth. Indeed, the increase of the total working pressure, within the studied range, increases the reactivity of the plasma due to higher electron density,³⁹ higher number of collisions, and higher radiation intensity (attested by more intense light emission). These three phenomena boost the degradation rate of the organometallic precursor and the subsequent nanoparticle germination (nucleation of iron clusters); they also enhance the probability of N-species to react with seed particles. Once the seed particles are formed, they are

exposed to the reactive plasma environment where several physical, chemical and thermal mechanisms may occur, including ion etching, oxidation, nitridation and heating,^{19,40,41}. The global composition indicates a high oxygen content (≈ 20 wt%) that is attributed to the release of oxygen from the reactor walls and/or from the carbon xerogel.^{19,42–44} The composition is not significantly affected by the pressure except at 6mTorr where higher O-content is observed, that may be attributed to some remains of the precursor. However, the XPS analysis revealed the modification of the oxygen localisation that is more bound to iron at higher pressure. This indicates that the higher reactivity of the plasma at high pressure promotes the incorporation of oxygen into the Fe_xN nanoparticles to form oxynitrides.^{45–47} X-ray and electron diffraction patterns does not indicate the presence of iron oxide phases; this suggests that oxygen is incorporated in thin amorphous oxide layer, or, more probably, in the nitride structure. Moreover, the increase of the working pressure induces a higher heat exchange (by collisions) which results in the rise of the sample surface temperature and consequently allow for a higher mobility for iron species to diffuse and form larger and more crystallized nanoparticles.^{41,48} The increase of the crystallization at higher working pressure is in agreement with a recent work from Kramer *et al.*⁴⁸ which suggested that the crystallization of nanoparticles directly depends on the plasma reactivity.

Magnetic properties analysis

The magnetic properties of all synthesized samples were characterised by vibrating sample magnetometry (VSM) at temperatures from 5 to 300 K, with the applied magnetic field (H) intensity up to ± 9 T (**Figure 5**). The magnetic moment values are reported in electromagnetic units (emu) per mass unit of sample (which contains about 10 wt.% of iron). Within the four samples synthesized at different working pressures, we observe the following trends: (i) the total magnetic moment (M) looks as a mixture of a ferromagnetic signal as evident from the hysteretic behaviour at low field (as shown in the insets) and a paramagnetic and/or superparamagnetic signal, as evident from the overall

Langevin-like shape of the magnetization curves at high field. For the samples synthesized at low pressure, the paramagnetic/superparamagnetic signal dominates, while a stronger ferromagnetic behaviour dominates in the samples synthesized at higher working pressure.

Among the multiple stable Fe-N nitrides phases, the α'' -Fe₁₆N₂, γ' -Fe₄N and ϵ -Fe₃N exhibit ferromagnetism properties,⁴⁹ while Fe₂N does not present ferromagnetic behaviour.^{26,27} The presence of a ferromagnetic phase, as indicated by magnetometry analysis, is consistent with XRD and TEM results pointing out the formation of the ϵ -Fe₃N phase, which is known to be ferromagnetic.

From the analysis of M vs H curves, we can extract some useful quantitative parameters to quantitatively compare of the ferromagnetic properties of each sample. The coercivity H_c (the applied field required to reach the zero net moment), and the remanence M_r (the magnetic moment at zero applied field), can both be trivially extracted from the hysteresis loops (as shown in the insets of Figure 5).

The derivation of the saturation magnetization (M_s) from the experimental curves is indirect, since the saturation regime is not achieved because of the persisting paramagnetic signal which is superposed over the ferromagnetic signal. One way to extract M_s , is to fit the curve with the so-called “Law of Approach to Saturation” (LAS)^{50,51} based on the following equation:

$$M = M_s \left[1 - \frac{a}{H} - \frac{b}{H^2} \right] + \chi H \quad (1)$$

this equation is valid for a pure ferromagnet, where M_s is the saturation magnetization, a is a parameter related to magnetic hardness, b is a parameter related to anisotropy, and χ is the total diamagnetic and paramagnetic susceptibility and H is the magnetic field. Here we will only focus on comparing the obtained M_s values.

Since the equation (1) assumes a linear χH term, therefore the relation is only valid for curves where $M(H)$ is linear, i.e. at sufficiently large magnetic field and temperature (here above 50 K). The values of H_c , M_s and M_r extracted from the $M(H)$ loop curves are plotted in **Figure 6** as a function of the

plasma synthesis pressure and for various measurement temperatures. The fitting parameters are given in supplementary information.

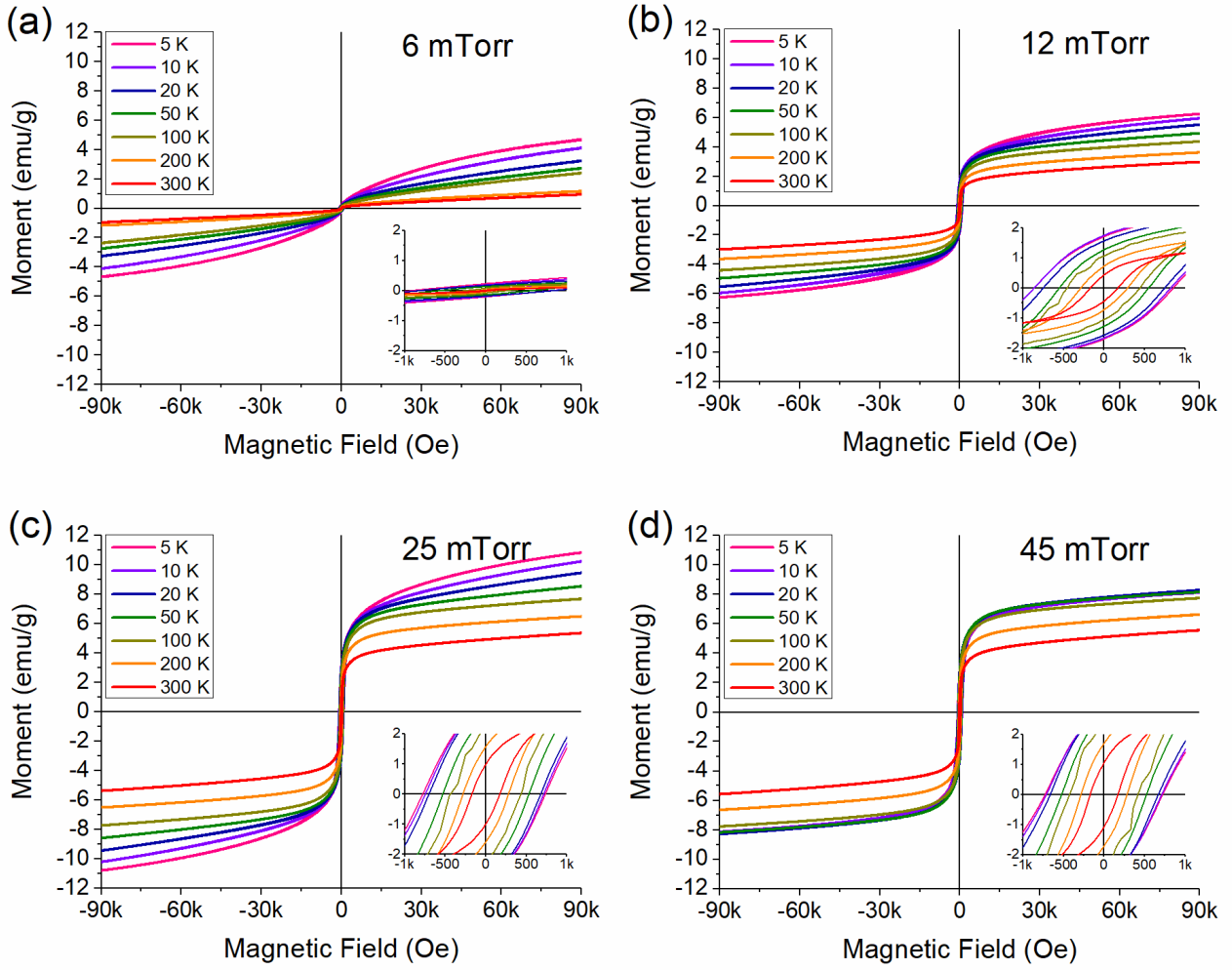


Figure 5. $M(H)$ loop curves of $\text{Fe}_3\text{N}/\text{C}_{\text{XG}}$ treated at (a) 6, (b) 12, (c) 25 and (d) 45 mTorr.

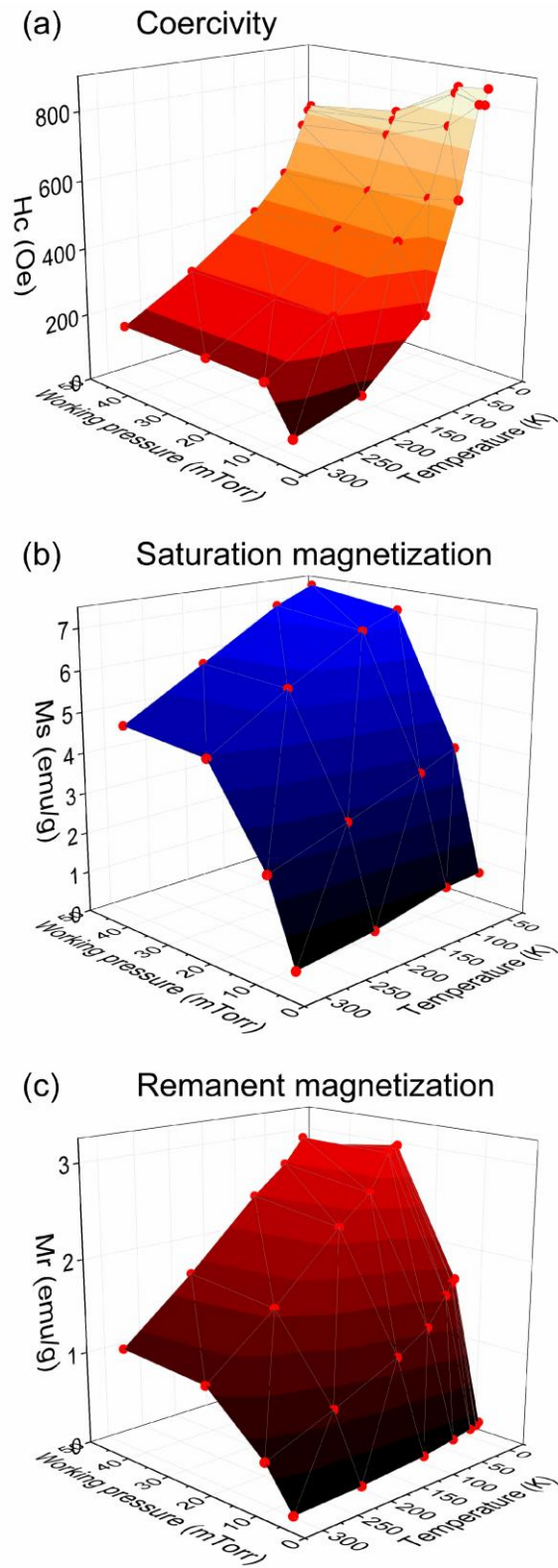


Figure 6. Evolution of (a) the coercivity H_c , (b) the saturation magnetization M_s and (c) the remanent magnetization M_r as a function of the plasma treatment pressure (6-45 mTorr) and the measurement temperature (5-300 K).

Overall, the plasma pressure results to strongly influence the magnetic properties. At 45 mTorr the nanocomposite exhibits the highest M_s of 7.4 emu/g at 50 K and above 4.5 emu/g at room temperature (Figure 6b). At the lowest working pressure (6 mTorr) the M_s value drops to below 1 emu/g with almost no temperature dependence. The sample synthesized at the 45 mTorr also show a remanent magnetization at 5 K of $M_r=3$ emu/g (Figure 6c). This last disappears in the samples synthesized at lower working pressure.

Previous work reported saturation magnetization values ranging from 15.2 to 130 emu/g at 5 K,^{11,49,52,53} with bulk ϵ -Fe₃N having saturation magnetization of 133 emu/g.^{37,54} Taking into account that our samples contained about 10% FeNx by mass, our measured saturation magnetization values are consistent with the values from the literature.

The magnetic properties of ϵ -Fe₃N have been investigated in several previous works.^{26,36,37,49} The magnetic moment arises from unbalanced distribution between spin-up and spin-down states, mostly coming from Fe 3d and N 2p in ϵ -Fe₃N.^{36,55} Panda *et al.* and Vinod *et al.*^{36,55} describe electron exchange giving the Fe-N bond a covalent behaviour but, at the same time, nitrogen acts as an electron donor, enhancing an ionic-type bonding. As a consequence, the number of unpaired *d* electrons diminishes, lowering the magnetization of ϵ -Fe₃N compared to α -Fe. It is known that the magnetization strongly evolves with the nitrogen content, lattice expansion, particle size and crystalline structure.^{22,27,36,49,53} Reducing the pressure in the plasma synthesis leads to the reduction of both the crystalline state, from well crystallized to amorphous nanoparticles, and the particle size. These in turn affect the unbalanced charge distribution between spin-up and spin-down states, responsible for the net magnetic moment, and ultimately for the decrease of the saturation magnetization.

Finally, the larger crystallite size at high pressure would favour the ferromagnetism because of the lower alteration of the unbalanced charge distribution between N 2p and Fe 3d states; one would thus expect that the increase of oxygen content in the nanoparticles synthesized at high pressure (see Figure

4) should result in the reduction of the M_s .^{56,57} Surprisingly, this effect is not observed, meaning that the higher crystallinity dominates over the oxidation. This might be due to the fact that the oxidation affects the nanoparticle surface which does not sensibly contribute to the magnetic properties.

Application to the pervaporative dehydration of an ethanol/water mixture

Pervaporative dehydration is an effective and energy-efficient method in which a membrane is used to separate the constituents of an azeotropic composition (*e.g.* solvent and water). This method is frequently used for ethanol dehydration because this separation is difficult to achieve by conventional separation processes. The membrane is generally composed of a permselective polymer (alginate, chitosan) which improves the performance of the membrane. Recent works have focused on membrane loading with the addition of magnetic nanoparticles in order to increase the water diffusivity within the membrane, while keeping a constant (or even decreasing) ethanol diffusivity.^{58,59}

The pervaporative membrane performance depends on (i) the *transport properties* and (ii) the *separation effectiveness*. The *transport properties* are measured with regard to the flux (J_N , in $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), the permeation coefficient of each species (ethanol and water here, P_{water} and P_{EtOH} measured in Barrer), the diffusion coefficients (D_{water} and D_{EtOH} in $\text{cm}^2\cdot\text{s}^{-1}$), the solubilities (S_{water} and S_{EtOH} in $\text{cm}^3_{\text{sccm}}\cdot\text{cm}^{-3}\cdot\text{cmHg}^{-1}$) and the selectivity coefficient (S_c). The *separation effectiveness* is measured through the separation factor $\alpha_{\text{H}_2\text{O}/\text{EtOH}}$ and the pervaporation separation index (PSI in $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$). The methodology to determine the parameters and the complete meaning of the coefficient are given on supplementary information. The separation factor $\alpha_{\text{H}_2\text{O}/\text{EtOH}}$ is a measure of the quality of the separation that the membranes provides⁵⁸ and is defined as:

$$\alpha_{AB} = \frac{y_A/y_B}{x_A/x_B} \quad (2)$$

where x_A and x_B are the weight fraction of components in the feed solution in wt.%, and y_A and y_B the weight fraction of components in the permeate (in wt.%). In order to compare the separation efficiency

of the investigated membranes, the pervaporation separation index (PSI) expressed by following equation was used:

$$PSI = J(\alpha_{AB} - 1) \quad (3)$$

where J is the total permeate flux and α_{AB} is the separation factor. The parameters evaluated for the pristine and hybrid sodium alginate membranes filled with different amounts of $\text{Fe}_x\text{N}/\text{C}_{\text{XG}}$ are shown in **Table 3**, **Figure 7** and **Figure 8**.

Table 3. Estimated transport and performance parameters for alginate membranes filled with $\text{Fe}_x\text{N}/\text{C}_{\text{XG}}$ amounts.

$\text{Fe}_x\text{N}/\text{C}_{\text{XG}}$ content (wt.%)	0	1	3	5	10
J_{N} ($\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	0.71	1.03	1.42	1.65	2.15
P_{water} ($\times 10^5$ Barrer)	4.83	18.83	20.48	22.5	26.25
P_{EtOH} ($\times 10^5$ Barrer)	0.23	0.87	0.94	1.24	5.07
D_{water} ($\times 10^7$, $\text{cm}^2\cdot\text{s}^{-1}$)	1.44	9.28	12.24	19.26	25.61
D_{EtOH} ($\times 10^7$, $\text{cm}^2\cdot\text{s}^{-1}$)	0.22	0.48	0.42	0.42	1.25
S_{water} ($\text{cm}^3_{\text{STP}}\cdot\text{cm}^{-3}\cdot\text{cmHg}^{-1}$)	335.4	202.9	167.3	116.8	102.5
S_{EtOH} ($\text{cm}^3_{\text{STP}}\cdot\text{cm}^{-3}\cdot\text{cmHg}^{-1}$)	104.5	183.0	224.0	293.7	406.1
S_{c}	21.0	21.64	21.78	18.14	5.18
$\alpha_{\text{water/EtOH}}$	26.65	57.88	65.42	28.84	12.15
PSI ($\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$)	18.2	58.6	91.5	45.9	24.0

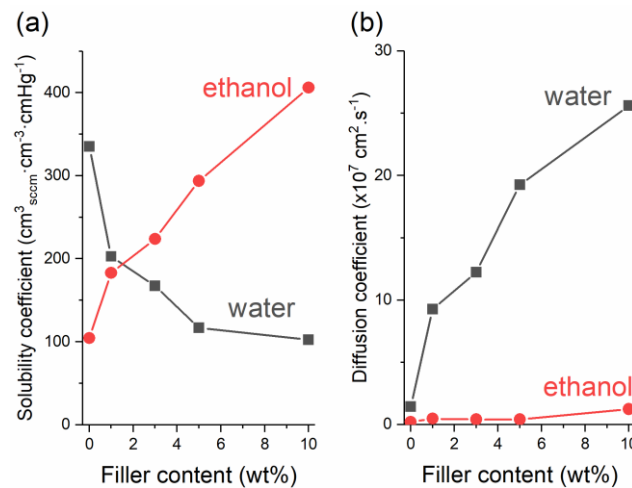


Figure 7. (a) Solubility and (b) water/ethanol diffusion coefficients in hybrid alginate membranes as a function of the $\text{Fe}_x\text{N}/\text{C}_{\text{XG}}$ filler loading.

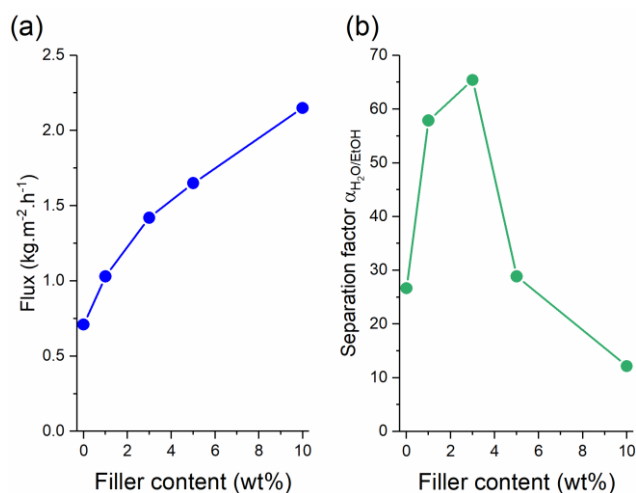


Figure 8. (a) Water/ethanol flux and (b) separation factor in hybrid alginate membranes as a function of the Fe_xN/C_xG filler loading.

From the above results, the bare sodium alginate membrane appears to be moderately selective and applicable in the pervaporative dehydration of ethanol with a separation factor of 26.6 and a pervaporation separation index of 18.2 kg·m⁻²·h⁻¹. The addition of the Fe_xN/C_xG filler into the alginate membrane has a positive impact on its separation properties. The water solubility in the membrane decreases with the filler content and reaches down to 3 times smaller values respect to the bare membrane (Figure 7a), and the water diffusion coefficient sensibly increases with the filler loading (Figure 7b) and reaches an 18 times larger value respect to the bare membrane with a filler loading of 10 %w/w. Oppositely, for ethanol molecules, the solubility coefficient increases with the filler content (Figure 7a) and the ethanol diffusion coefficient only slightly increases with the filler loading (Figure 7b). Results show that the Fe_xN/C_xG filler promotes the separation process of the ethanol/water mixture. This effect is attributed to the magnetic properties of iron nitride nanoparticles. Specifically, each molecule has a specific magnetic characteristic due the spin and orbital magnetic moments of their electrons and nuclei. Toledo *et al.*⁶⁰ studied the influence of a magnetic field on the interactions of the water molecules using theoretical calculations and the alterations on the physico-chemical properties, through experimental measures of vaporization enthalpy, viscosity and surface tension. They noticed that the magnetic field weakened the stronger intra clusters hydrogen bonds, breaking the larger clusters on the smaller ones with stronger inter cluster hydrogen bonds. Smaller clusters of

water molecules can easier penetrate through the membrane and thus may be responsible for the more effective separation of the water/ethanol mixture..

The water/ethanol flux in the membrane clearly increases with the $\text{Fe}_x\text{N}/\text{C}_{\text{XG}}$ filler content (Figure 8a). This is ascribed to free volume created by the filler into the polymer matrix, which facilitates the transport of molecules. While the flux constantly increases with the $\text{Fe}_x\text{N}/\text{C}_{\text{XG}}$ loading, the separation factor value only increases up to 3 %w/w loading (Figure 8b). The reduction of the membrane selectivity at high loading, is ascribed to the excessively high diffusion of water and ethanol species. The best result is thus obtained for alginate membrane filled with 3%w/w of $\text{Fe}_x\text{N}/\text{C}_{\text{XG}}$ allowing for a separation factor of 65.4, a *PSI* of 91.5, $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and a relatively high flux of $1.4 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, demonstrating an effective membrane for ethanol dehydration, based on cheap and non-toxic materials.

CONCLUSION

Iron nitride nanoparticles have been synthesized by ICP plasma degradation of iron acetylacetonate on a carbon xerogel as support. A series of $\text{Fe}_x\text{N}/\text{C}_{\text{XG}}$ samples have been investigated by varying the pumping rate, to tune the working pressure in the $\text{Ar}:\text{NH}_3$ plasma from 6 to 45 mTorr. The synthesis pressure is found to significantly affect the nanoparticle nucleation rate and crystallinity of the Fe_xN nanoparticles thus finally affecting their ferromagnetic properties. The $M(H)$ loop curves indicate that the coercivity, the remanent magnetization and the saturation magnetization increase with the plasma treatment working pressure.

Due to its versatility, the proposed plasma-based methodology can be easily adapted to other metal precursors and substrates. In addition, it has a rather low energetic and environmental impact (solvent-free). Finally, the optimized $\text{Fe}_x\text{N}/\text{C}_{\text{XG}}$ composite was applied as an effective filler for alginate membrane, for pervaporative ethanol dehydration. At the optimum loading of 3 %w/w, the performance of a pristine alginate membrane could be considerably enhanced, in term of selectivity,

separation index and flux. These results demonstrate that the synthesized magnetic material is an efficient, cheap and non-toxic filler for such hybrid membranes.

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SUPPORTING INFORMATION DESCRIPTION

The S.I. describe the pervaporation measurement setup and provide a minimum of theoretical background on the method. The fitting parameter of magnetic measurement are given in a separated excel file.

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