

1 **Polyaniline (PANI): an innovative support for sampling and removal of VOCs in air matrices**

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8 9 **Abstract**

10 Polyaniline (PANI)-based materials for both removal and sampling of volatile organic compounds
11 (VOCs) from air by rapid adsorption/desorption processes have been developed. The polymer was
12 synthesized in form of emeraldine as both salt and base using different synthetic approaches, a
13 traditional one and a “green” one. VOCs adsorption/desorption efficiency was evaluated for all the
14 materials analyzing the desorbed VOCs fractions by GC/MS technique and obtaining results similar
15 to the presently adopted method employing commercial activated carbon. Most important, in this
16 work it has been demonstrated for the first time that the use of PANI-based sorbents allowed the
17 substitution of the toxic CS₂, recommended in official methods, with the less hazardous CH₃OH as
18 the VOCs extraction solvent. Moreover, a complete regeneration of the polymers could be realized
19 by a few rapid washing steps. Finally, the best PANI-based material was subjected to recycling tests
20 thereby showing a high adsorption/desorption efficiency retention up to four runs.

21
22 **Keywords:** polymers, sampling, VOCs, air matrix, pollutants abatement

23 24 **1. Introduction**

25 VOCs are defined as organic compounds having a vapor pressure greater than 10⁻¹ Torr at 25°C and
26 760 mmHg [1]. VOCs sources are numerous and various ranging from industrial plants to aircrafts,
27 vehicles, etc. and their emission negatively affects indoor and outdoor quality air because of their
28 high toxicity, having negative consequences on human health, such as sensory irritation, increase in
29 allergies and many other symptoms known as Sick Building Syndrome (SBS). For this reason,
30 recently, analytical and environmental chemistry has paid attention to VOCs determination in order
31 to monitor environmental pollution and take care of human health.

32 Even though many strategies have been developed to VOCs abatement [2], the use of adsorbent
33 materials results to be the most effective.

34 The required features for a good adsorbent include high surface area and large pore volume. As a
35 consequence, activated carbons are the best candidates despite some disadvantages, such as high
36 pressure drop over the adsorbent bed, a gradual reduction of adsorption activity after a certain time,
37 difficulty in regeneration. More recently, Scholten *et al.* proposed the use of electrospun
38 polyurethane fibers for VOCs adsorption [3]. These materials showed high affinity toward toluene
39 and chloroform and were easily regenerated.

40 The use of intrinsically conducting polymers (ICPs), in particular polyaniline (PANI), as sensing
41 materials for VOCs detection has been deeply investigated [4]. However, to the best of our
42 knowledge, these materials have not been investigated for sampling or abatement/adsorption
43 purposes and no comparison with activated carbon has been done.

44 Among ICPs, PANI is the most investigated one thanks to its unique properties and features, such
45 as ease of synthesis, environmental stability, high conductivity, interesting redox properties that
46 make it a good candidate for application in electronic and optical devices [5].

47 Although PANI can exist in different oxidation states, ranging from leucoemeraldine (the totally
48 reduced form) to pernigraniline (the totally oxidized form) through emeraldine (the half-oxidized
49 form), only the half-oxidized half-protonated form of polyaniline, called emeraldine salt, is stable
50 and conductive therefore the most investigated one.

51 The most popular synthetic procedure for PANI preparation deals with the oxidative polymerization
52 of aniline monomer by stoichiometric hazardous oxidants, such as KMnO_4 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$,
53 metals in high oxidation states, etc. If on the one hand this approach leads to a polymer
54 characterized by good chemico-physical properties, on the other hand the production of
55 toxic/carcinogenic co-products (e. g., benzidine and *trans*-azobenzene) and inorganic waste (sulfate,
56 chromate, metals in high oxidation state, etc.) in large amount limit its real application.

57 In order to avoid the production of toxic/mutagen substances and inorganic waste, we have recently
58 investigated the possibility to produce PANI by an innovative “green” approach based on the
59 oxidative polymerization of *N*-(4-aminophenyl)aniline using hydrogen peroxide or molecular
60 oxygen as the oxidizing agents in the presence of proper catalysts [6-9]. This innovative approach
61 leads to H_2O as the unique co-product and totally eliminates the production of toxic species
62 simplifying the polymers post treatment.

63 Inspired by our experience in the field of environmentally friendly synthesis of PANI [6] and its
64 application in different sectors [7-9], we decided to prepare and employ for the first time
65 polyaniline as a substitute of activated carbon for VOCs sampling and removal. GC/MS is a good
66 and rapid analytical technique for VOCs determinations, hence it was chosen to analyze the
67 desorbed organic fractions from PANI-based cartridges. Herein we report our recent achievements

68 either in terms of adsorption/desorption efficiency or easy and fast regeneration of the material after
69 a 4-run recycling, suggesting an alternative strategy in capturing VOCs in place of commercial
70 activated carbon.

71 Some of the official analytical methods available for VOCs analysis recommend the use of CS₂ as
72 the solvent extraction and activated carbon as the adsorbent support, although other popular
73 polymeric sorbents exist, such as Tenax or Chromosorb [10]. Although many drawbacks are related
74 to the use of CS₂ (high toxicity, air pollutant, analytical interferences, etc.), currently it is still
75 employed in numerous sectors. In the present work a less toxic solvent, CH₃OH, was chosen as the
76 solvent extraction.

77 **2. Experimental section**

78 **2.1. Reagents, standards and instruments**

79 All chemicals and sampling glass tubes were purchased from Sigma Aldrich. Chemicals were used
80 as received without further purification.

81 A standard solution (certified reference material, CRM) of VOCs 1000 µg/ml each (Table 1) in
82 carbon disulfide and an internal standard solution (CRM) containing bromochloromethane,
83 chlorobenzene (d5), 1,4-difluorobenzene, 4-bromofluorobenzene 1000 µg/ml each in carbon
84 disulfide were purchased by CPAchem and used for GC/MS calibration.

85 A standard solution (RM) of VOCs (Table 1) 1000µg/ml each in methanol was purchased by Ultra
86 Scientific and an internal standard solution (RM) of bromochloromethane, chlorobenzene (d5), 1,4-
87 difluorobenzene, 4-bromofluorobenzene 1000µg/ml each in methanol was purchased by O₂Si and
88 used for GC/MS calibration.

89 A cylinder containing a mixture gaseous VOCs (Table 1) in nitrogen having a nominal
90 concentration of about 1 ppmv was purchased by SIAD and used for loading support materials in
91 glass tubes. Infrared spectroscopy (FT-IR) spectra of KBr dispersed samples were recorded on a
92 JASCO FT/IR-410 spectrophotometer in the 500–4000 cm⁻¹ range. UV–Vis spectra were recorded
93 on a Hewlett Packard 8453 spectrophotometer using *N,N*-dimethylformamide (DMF) as the solvent.
94 X-ray powder diffraction (XRPD) analyses were performed using a Rigaku D IIIMAX horizontal-
95 scan powder diffractometer with Cu K α radiation. SEM images were recorded by a SEM-LEO
96 1430 microscope. Porosity measurements were performed by a Sorptometer Instrument (Costech
97 mod. 1042) *via* single-point method. Before measurements, the samples were pretreated at 130°C
98 for two hours. GC/MS analyses were performed on a GC/MSD with Triple-Axis Detector Series
99 5975C Agilent Technologies using a Thermo Scientific TR-5MS (length=60m; i.d.=0.25mm;
100 film=1.0µm) column.

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102 **2.2. Materials preparation**

103 **2.2.1. PANI1 and EB1 preparation (traditional method)**

104 PANI1 was prepared according to a method as reported in the literature [11]. More in detail, in two
105 separated flasks 1.0 g (10.76 mmol) of aniline was solubilized in 10 mL of HCl 10 M and 4.4 g
106 (19.3 mmol) of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 15 mL of deionized water. Both the solutions were cooled at 4°C for
107 30 minutes. Then, the oxidant aqueous solution was added dropwise to the solution containing
108 aniline chloride and the polymerization reaction took place immediately. After 6 h, acetone was
109 added in order to stop the reaction and a dark green solid was collected by filtration, washed several
110 times by water and acetone and dried under air. The obtained product, characterized by
111 spectroscopic and diffractometric techniques, was identified as emeraldine salt (PANI1) [6-8, 11].
112 A 72% polymerization yield was calculated.

113 Part of the obtained PANI1 was converted into its corresponding base (emeraldine base, EB1) by
114 the deprotonation process as described below.

115 500 mg of PANI1 were put in contact with 20 mL of NH_4OH 1 M (20 mmol) for 24 hours. Then,
116 the obtained dark blue powder was collected by filtration, washed several times by water until the
117 mother liquors became neutral and dried under air. This product, characterized by spectroscopic and
118 diffractometric techniques, was identified as emeraldine base (EB1) [6-8, 12].

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120 **2.2.2. PANI2 preparation (“green” method)**

121 PANI2 was prepared following a synthetic procedure similar to that reported elsewhere [8]. Briefly,
122 4 g of *N*-(4-aminophenyl)aniline (43.5 mmol) were dissolved in 800 mL of 0.8 M HCl. Then, 22 ml
123 of H_2O_2 30% (21.8 mmol) were quickly added under stirring followed by addition of 16.2 mg of
124 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.06 mmol). The mixture was stirred for 24 hours at room temperature. Finally, a dark
125 green product was collected on a filter, abundantly washed with deionized water and acetone, until
126 the washings became colorless and dried in air. The obtained product, characterized by
127 spectroscopic and diffractometric techniques, was identified as emeraldine salt (PANI2) [6-8, 11].
128 A 86% polymerization yield was calculated.

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130 All the synthetic procedures reported in sections 2.2.1. and 2.2.2. were repeated three times. The
131 reaction yields differed less than 5% and each datum reported in the present work has been
132 calculated as mean value of the three data.

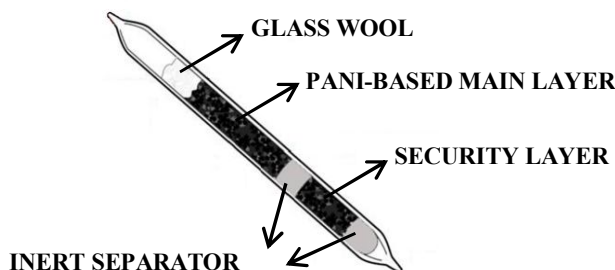
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136 **2.3 Sorbent tubes preparation**

137 In each sampling glass tube the carbon-based main layer was replaced with a few milligrams of
 138 PANI-based material (320 mg of PANI1, 308 mg of EB1 and 310 mg of PANI2), whereas the
 139 security layer, made of activated carbon, was maintained as a check breakthrough (Figure 1).



147 Figure 1: Glass tube scheme.

150 **2.4 Adsorption/desorption experiments**

151 Each tube was properly connected to a cylinder containing a mixture of VOCs (Table 1) as gases
 152 and loaded by a flow rate of 50 mL/min for 10 minutes, properly monitored by a flow-meter.

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VOCs
1,1 dichloroethene
dichloromethane
Ethane, 1,1,2-trichloro-1,2,2-trifluoro-
trans 1,2 dichloroethene
1,1 dichloroethane
cis 1,2 dichloroethene
Chloroform
Ethane, 1,1,1-trichloro-
Ethane, 1,2-dichloro-
Carbon tetrachloride
Benzene
Trichloroethylene
Propane, 1,2-dichloro-
Toluene
Ethane, 1,1,2-trichloro-
Tetrachloroethylene
Benzene, chloro-
Ethylbenzene
m&p Xylene
o-Xylene

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Table 1: List of investigated VOCs.

155 Thereafter, the two layers were separated. The PANI-based main layer was occasionally stirred with
156 1 mL of methanol for 30 min, whereas the security layer was extracted with 1 mL of CS₂ according
157 to official methods [12]. The organic extracts were analyzed as reported below (section 2.5).

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159 2.5 VOCs analysis by GC/MS technique

160 All the extracted fractions were processed by the following GC/MS conditions and quantified by the
161 internal standard method.

162 Oven program: 40°C for 8 min; then 4°C/min to 100°C for 0 min; then 15°C/min to 320°C for 9
163 min; then 40°C/min to 330°C for 1 min - Run Time 47.917 min. Helium was used as the gas carrier.
164 SS Inlet: Mode Splitless. Inlet temperature: 250°C. Flow 1.2mL/min. MSD condition: acquisition
165 SIM-mode. MSZones: MS Source: 250 C MS Quad: 150 C.

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167 2.6 Regeneration tests

168 PANI1, used as reported above, was regenerated and reused up to five times as described below.
169 After the solvent extraction process PANI1-based main layer was washed three times with
170 methanol, dried under air and used to fill a new glass tube, whereas unused carbon-based security
171 layers were always employed. The adsorption/desorption procedure, reported in section 2.4, was
172 repeated and the new extracts analyzed as reported in section 2.5.

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174 3. Results and discussion

175 3.1 Materials Characterization

176 Emeraldine salts (PANI1 and PANI2) and base (EB1) were characterized by different techniques.
177 Figure 2 reports the FT-IR and UV-vis spectra of PANI1, PANI2 and EB1 respectively.

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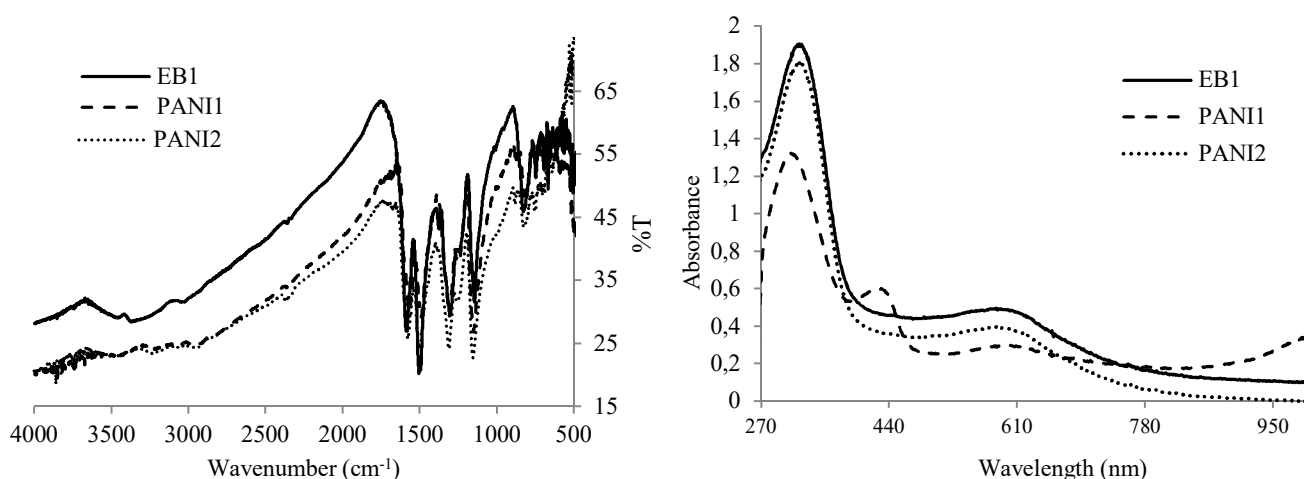


Figure 2: (Left) FT-IR and (right) UV-vis spectra of PANI1, PANI2 and EB1 respectively

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190 Infrared spectroscopy is probably the most powerful technique for ICPs, especially for polyaniline
191 characterization, as it allows to obtain information about the oxidation state of the polymer and its
192 conjugation level [13]. The absorption bands of all the samples lied in the same region and with
193 similar intensities except for marginal differences. More in detail, the band at 1570 cm^{-1} can be
194 assigned to the C=C stretching of the quinoid rings, whereas the stretching vibration mode for the
195 benzenoid rings is responsible for the two bands at around 1498 cm^{-1} and 1484 cm^{-1} . The ratio
196 between the bands at 1570 cm^{-1} and 1498 cm^{-1} , that is diagnostic to estimate the oxidation state of
197 the polymer, is around 1 thus confirming that polyaniline was obtained in form of emeraldine,
198 which means equal amounts of amino-benzenoid and imino-quinoid rings [15]. The bands at 1310
199 cm^{-1} and 1245 cm^{-1} are related to C-N and C=N stretching modes, whereas in-plane and out-of-
200 plane C-N bending vibrations are responsible for the peaks at 1028 cm^{-1} and 890 cm^{-1} . The bands at
201 755 cm^{-1} and 695 cm^{-1} are assigned to the deformation vibration modes for the aromatic rings and
202 the one at 570 cm^{-1} is characteristic of 1,4 di-substituted benzenes [15, 16]. Finally, the broad band
203 from 2000 cm^{-1} to 4000 cm^{-1} is strictly related to the high conjugation level of the two materials and
204 is caused by overlapping of many vibration modes, especially the ones of amine and phenylene
205 diamine groups.

206 UV-visible spectroscopy is a useful tool for characterizing PANI-based materials because, as for
207 FT-IR technique, important information about polyaniline protonation level and oxidation degree
208 can be obtained. According to the literature [17], the electronic spectrum of polyaniline in its
209 emeraldine base form (EB1) shows two characteristic bands. Benzene rings lead to the first band at
210 around 300 nm, whereas the second one at around 570 nm is related to π - π^* transition of the
211 azaquinoid fractions in the polymeric chains. In the UV-vis spectrum of emeraldine salt (PANI1)
212 two new bands can be observed at about 420 nm and 1000 nm respectively. The first band is
213 associated to transitions involving polaron states (charged cation radicals), π -polaron, and polaron-
214 π^* transitions, whereas the second band could be related to different factors, such as a different
215 conjugation extension, change of conformation of the polymeric chains from coil-like to rod-like
216 [18], but also de-aggregation phenomena of polyaniline chains in solution [19]. Concerning PANI2,
217 a strong deprotonation effect by the solvent (DMF) was observed. In fact, the UV-vis spectrum of
218 PANI2 is totally similar to that of EB1. The different electronic spectra of the two emeraldine salts
219 can be related to a diverse protonation level of the two polymers that is a consequence of a lower
220 oxidation state for PANI2 than for PANI1.

221 The crystallinity content of all the synthesized materials was investigated by X-ray powder
222 diffraction (XRPD) and the obtained patterns are reported in Figure 3.

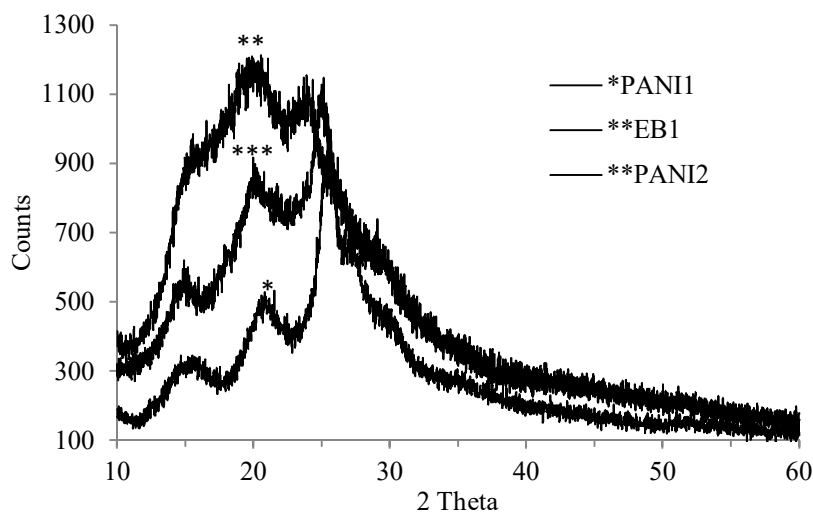


Figure 3: XRPD patterns of PANI1, PANI2 and EB1 respectively.

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Crystalline structure of polyaniline strongly affects its properties, such as electroconductivity, liquid and/or gases permeation, stress resistance and so on [20]. For this reason, an accurate investigation is crucial.

According to the pioneering investigations of Pouget, two classes of polyaniline can be distinguished by X-ray diffraction technique: *class I* and *class II* [21]. *Class I* is characterized by a crystalline structure for emeraldine salt (ES), whereas the insulating base form (EB), obtained after washing with ammonia solution, is essentially amorphous. On the other hand, *class II* exhibits a percentage of crystallinity both for ES and EB. Hence, it is clear from Figure 4 that the synthesized polymeric materials undoubtedly belong to *class I*.

On the basis of this evidence it is possible to affirm that the deprotonation process plays a key role in the reduction of the polymer crystallinity, whereas the presence of an acidic dopant (namely, HCl) in the salt causes additional hydrogen bonds and van der Waals interactions along and among the polymeric chains that could cause structural modifications.

Moreover, the synthetic method and the deprotonation process seem to effect also the materials morphology, as observed in SEM images (Figure 4).

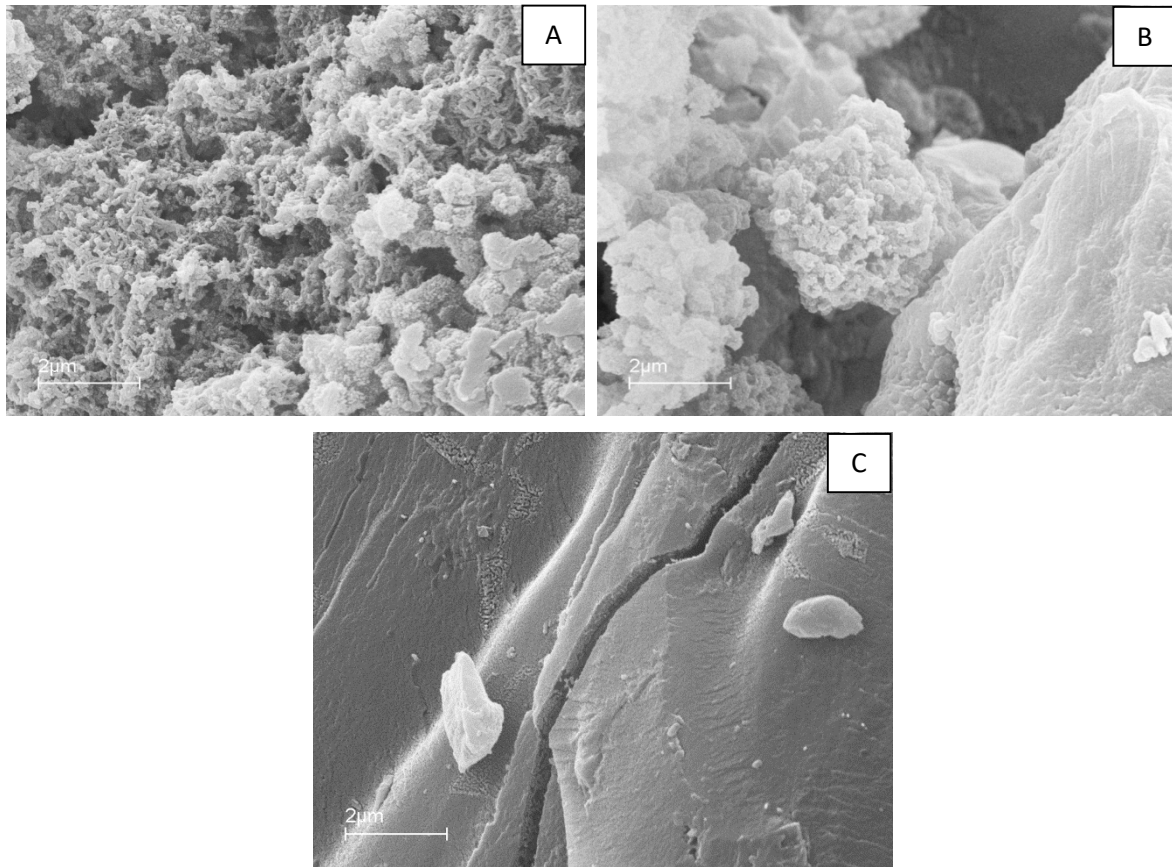


Figure 4: SEM images of PANI1 (A), EB1 (B) and PANI2 (C) respectively.

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In fact, if on the one hand PANI1, synthesized by a traditional way, led to a quite porous surface morphology characterized by rod-like structures generating micro-channels throughout the material (Figure 4 A), on the other hand PANI2, produced by a “green” synthetic approach, showed a highly compact morphology (Figure 4 B). These textural differences can be ascribed to the two different synthetic approaches. The traditional synthetic procedure, leading to PANI1, guarantees a high control of the polymeric chains growth differently from the innovative “green” way, employed to synthesize PANI2.

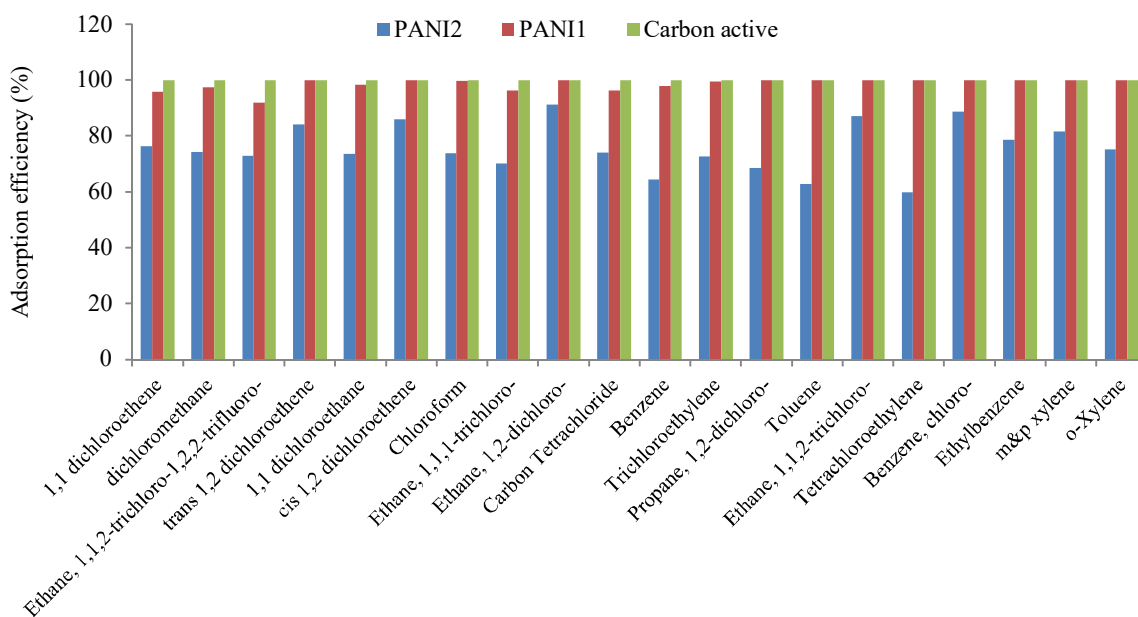
Furthermore, a collapse of the PANI1 microstructure was also observed after the deprotonation process, leading to a more compact and less porous material having morphological characteristics intermediate between PANI1 and PANI2 (Figure 4 C).

In order to get a deeper insight in the porosity of PANI1 and PANI2 the BET technique was adopted. Accordingly, porous PANI1 exhibited a porosity of 32.05 m²/g whereas, as expected, compact PANI2 resulted to be less porous with a porosity of 2.39 m²/g.

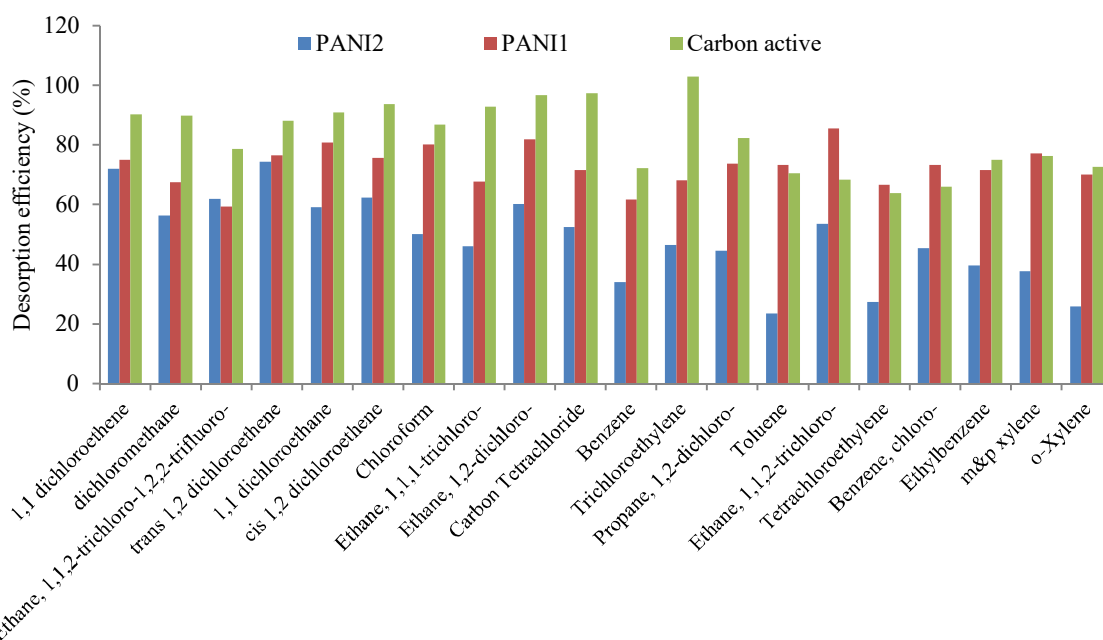
3.2 VOCs adsorption/desorption

It is worth to notice that in the present work many important VOCs, included in the current regulations and reported in official methods such as EPA-TO15, were investigated due to their renowned hazardousness for health and environment [1].

291 Figure 5 depicts adsorption/desorption efficiency of VOCs by PANI1 and PANI2 as well as a
 292 comparison with traditional activated carbon performances. These results were obtained analyzing
 293 by GC/MS technique the desorbed VOCs from the carbon-based security layers and PANI-based
 294 main layers for the adsorption and the desorption processes respectively. It is important to highlight
 295 that the comparison among PANI-based materials and activated carbon was carried out using
 296 different extraction solvents, namely CH₃OH for PANIs and CS₂ for activated carbon. The intention
 297 was to offer an alternative approach to the traditional methods typically recommending toxic CS₂ as
 298 the extraction solvent for VOCs monitoring by GC/MS technique.
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Figure 5: Percentage of (up) adsorption and (down) desorption efficiency towards VOCs for PANI1, PANI2 and activated carbon.

302 As it is possible to observe from Figure 5 (up), PANI1 exhibited a very high adsorption capacity
303 close to that of activated carbon (about 99%) for all the VOCs investigated. On the contrary, PANI2
304 showed lower performances, probably related to its low surface area and porosity.

305 Adsorption efficiency % was calculated as reported in Equation 1:

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307 (Eq. 1) Adsorption efficiency % = $100 - \left(\frac{\text{conc.VOC on security layer}}{\text{conc.VOC loaded on tube}} \cdot 100 \right)$

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309 Two types of adsorption process exist, namely physical adsorption and chemisorption based on the
310 interaction between adsorbate and adsorbent. Physical adsorption occurs when organic molecules
311 are held on the surface and in the pores of the adsorbent by the weak van der Waals forces of
312 attraction and is generally characterized by a reversible and rapidly established adsorption
313 equilibrium. To date, activated carbon is recognized as the most suitable adsorbent for VOCs
314 removal [22]. However, some authors pointed out some disadvantages related to the use of activated
315 carbon, strictly related to its flammability, difficulty to be regenerated, moisture sensitivity and so
316 on [23]. Therefore, new adsorbents have been investigated ranging from zeolites [24] to polymers
317 [25]. In this regard, the surprising ability of PANI1 to VOCs adsorption makes it a good candidate to
318 replace activated carbon. Moreover, the possibility to produce polyaniline in different shapes
319 (nanofibers, nanotubes, thin films, etc.) opens up new application perspectives for these materials in
320 this field.

321 Desorption efficiency % was calculated as reported in Equation 2:

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323 (Eq. 2) Desorption efficiency % = $\left(\frac{\text{conc.VOC on main layer}}{\text{conc.VOC loaded on tube}} \cdot 100 \right)$

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325 It is evident from Figure 5 (down) that also in this case PANI1 and PANI2 led to different
326 performances, higher for PANI1 than for PANI2. In general, for PANI1 a VOCs recovery in the
327 range 70-80% was estimated which is a little bit lower than that of activated carbon but, however, in
328 line with most of the official methods [12].

329 The desorption efficiency observed for PANI1 seems to follow averagely the trend: saturated
330 aliphatic compounds > unsaturated aliphatic compounds \approx aromatic compounds. The higher ability
331 of the polymer to retain unsaturated hydrocarbons more than saturated ones is assumed to be mainly
332 related to π - π interactions between PANI backbone and the C=C bonds present in the target
333 analytes. On the contrary, owing to the lack of π -electrons in the saturated molecules, the main

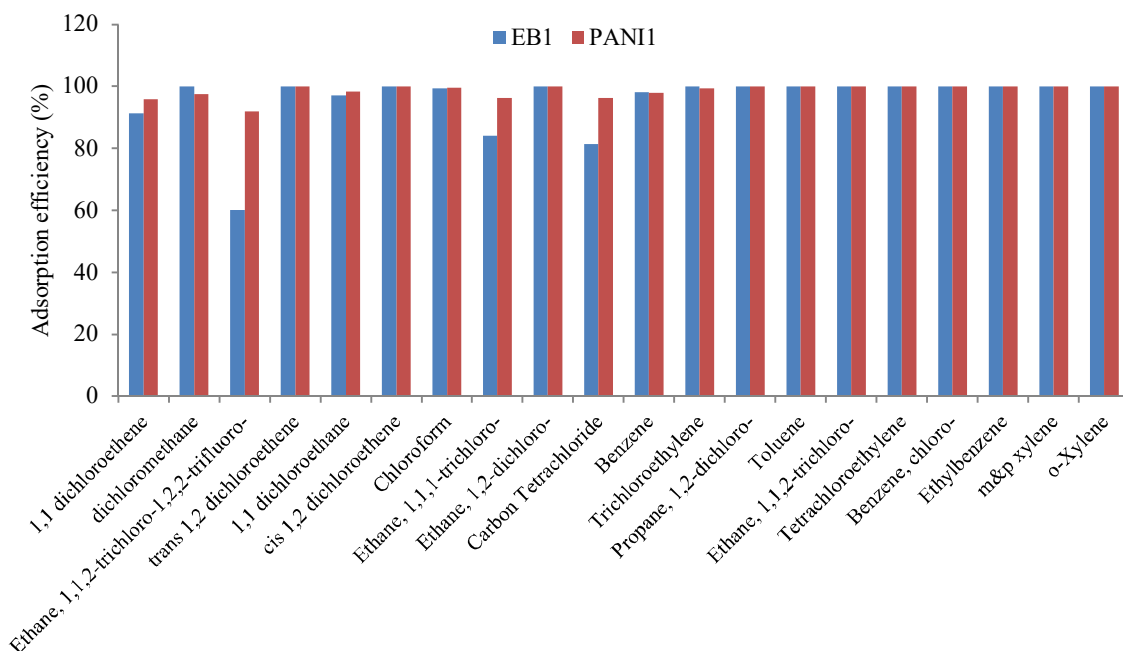
334 interactions between these species and the polymer are the weaker hydrogen bonding and van der
335 Waals forces of attractions.

336 More in detail, concerning the aromatic compounds, the presence of functional groups on the
337 benzene rings seems to play a role in the desorption efficiency of PANI1. -Cl and -CH₃ are typical
338 electron acceptor and donor groups, respectively, and PANI surface can serve as both an electron
339 donor and electron acceptor. As a consequence, the comparison between the desorption capacity of
340 the polymer and benzene and its derivatives (-Cl and -CH₃ substituted benzene) reveals some
341 differences, although a certain analytical variability has to be always taken into account.

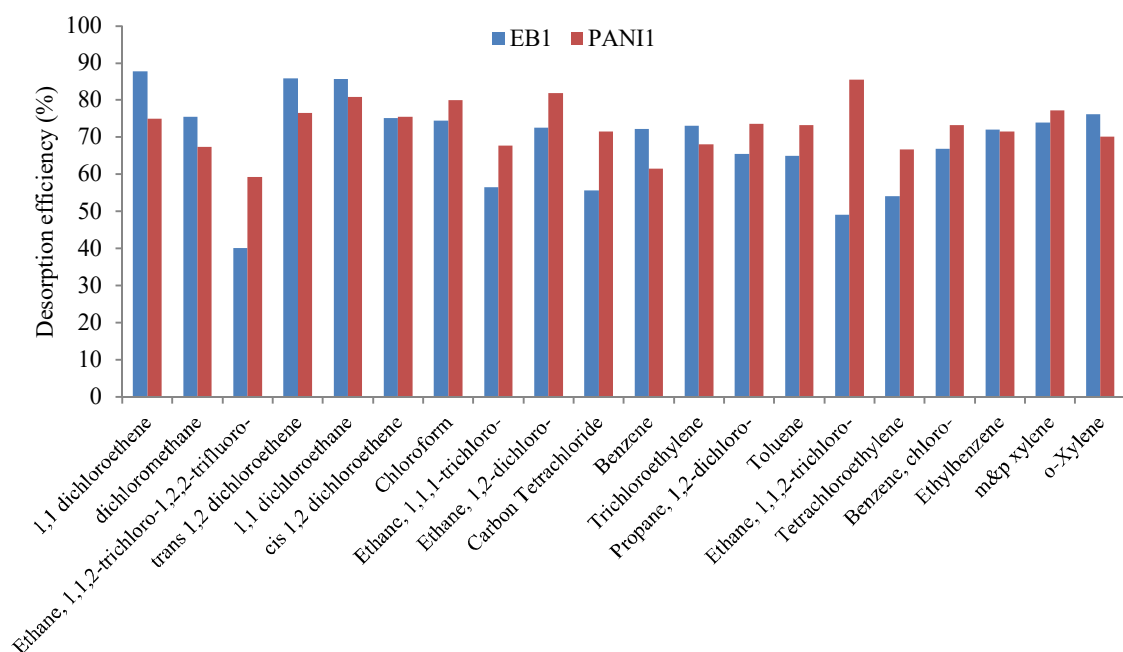
342 The presence of electronegative chlorine substituents plays a role also in the desorption of
343 unsaturated and saturated aliphatic hydrocarbons. However, although the increasing number of -Cl
344 groups seems to enhance the affinity for the polymeric absorber in the case of unsaturated
345 compounds, this trend is not maintained for -Cl substituted saturated species. Nevertheless, it is
346 known that this kind of analytes exhibits unusual effect on PANI surface owing to numerous and
347 various types of interaction between the polymer and these chlorinated compounds which also exist
348 as molecular pairs [26].

349 PANI2 displayed worst performances either for adsorption or desorption processes. Even though
350 many and complex factors can be involved, the differences observed between the two types of
351 polyaniline might be related to surface area, morphology and doping. All these aspects can play a
352 key role in the VOCs-PANI interactions.

353 In order to investigate the effect of dopant amount, the corresponding base of PANI1 (EB1) was
354 subjected to the same adsorption/desorption process as for PANI1. The results are reported in
355 Figure 6 and compared to those previously reported for PANI1.



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358 Figure 6: Percentage of (up) adsorption and (down) desorption efficiency towards VOCs for
 359 PANI1 and EB1.

360 In general, EB1 exhibited adsorption/desorption performances only slightly lower than those
 361 observed for the corresponding PANI1. Structural and morphological characterizations highlighted
 362 that EB1 had a surface morphology intermediated between those of PANI1 and PANI2 and the
 363 lowest doping level. Hence, it is possible to conclude that the protonation level is not responsible
 364 for the materials performances, whereas the main characteristic is represented by the surface
 365 morphology and porosity. Despite the marked advantages in terms of environmental impact offered
 366 by PANI2, this polymer results to be less active than PANI1 in the field of VOCs sampling and

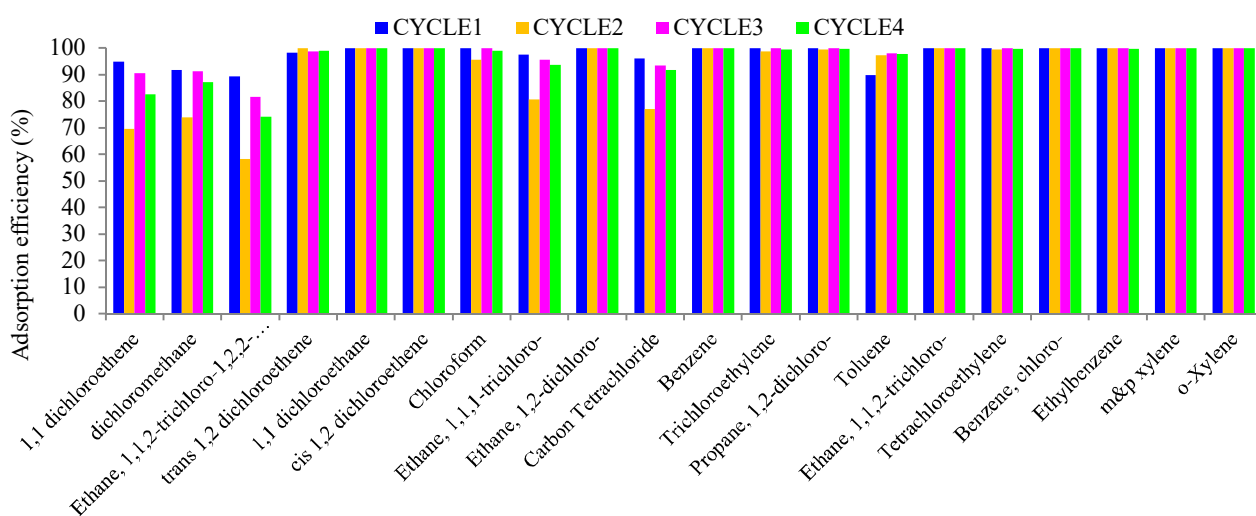
367 removal because of its poor chemico-physical properties. However, by properly tuning the reaction
 368 conditions, surface area and porosity, promising enhancements in PANI2 performance are arising
 369 (data not yet published) thus making this polymer a potential valid eco-friendly candidate.

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371 3.4. Regeneration tests

372 The possibility to regenerate and reuse adsorbent materials is fundamental for reducing waste
 373 production and process costs. Thanks to their extraordinary stability, PANI-based materials are
 374 promising candidates as recyclable adsorbents. On the basis of the best performances detected for
 375 PANI1, a 4-run recycling of the polymeric material (cycles 1-4) was carried out (Fig. 7).

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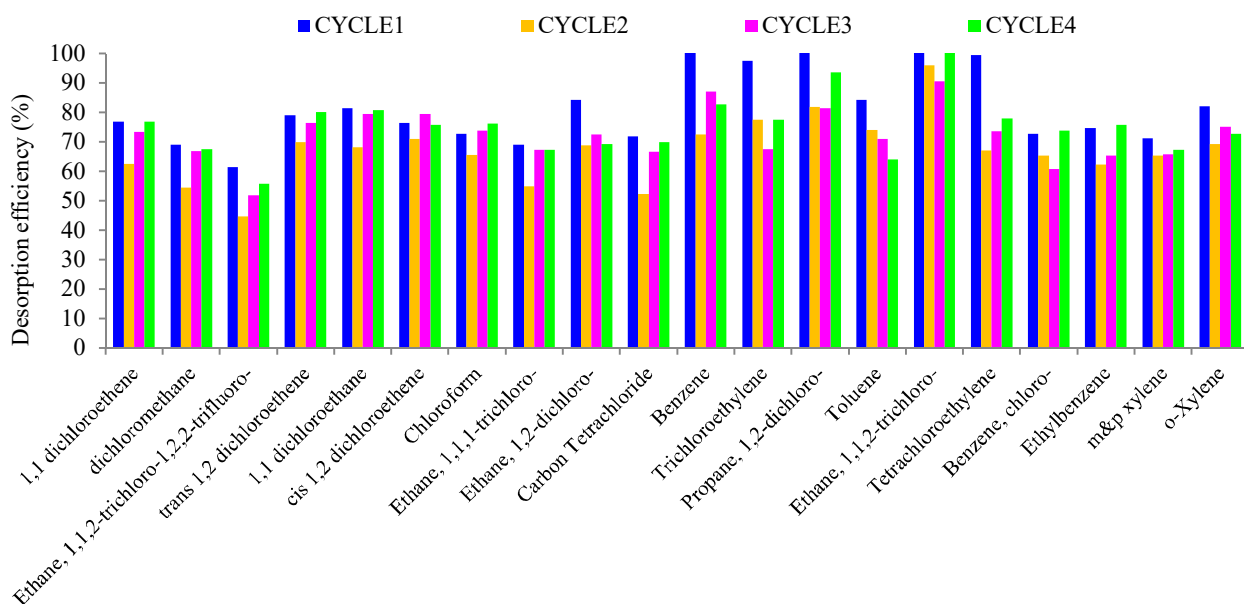


Figure 7: Percentage of (up) adsorption and (down) desorption efficiency towards VOCs for PANI1 under 4-run recycling (cycles 1-4).

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380 As it is possible to observe, a good reproducibility of the material performances was observed after
381 4-run recycling. The slight different behavior observed for some VOCs in the recycling tests
382 (desorption efficiency) can be presumably attributed to a series of analytical considerations, such as
383 intrinsic variability of the extraction method, intrinsic variability of instrumental reading, and not
384 least, gases mixing inside the cylinder. In fact, on the basis of these considerations, most part of the
385 reference methods assume a 20-30% bias variation [12].

386 Nevertheless, the high reproducibility of the repeated adsorption tests guarantees a good stability of
387 the polymer under the present conditions, hence promoting PANI1 as a good alternative to
388 traditional activated carbon.

389

390 **Conclusions**

391 The role of polyaniline (PANI)-based materials as good candidates for VOCs sampling and removal
392 from air matrices has been demonstrated for the first time. Surface area and porosity resulted to be
393 the most important parameters influencing the polymeric materials performances. Polyaniline
394 produced in its form of emeraldine salt by following a traditional synthetic way (PANI1) was found
395 to be the most activated material for VOCs adsorption/desorption processes. After a 4-run
396 recycling, PANI1 retained its high activity thus opening the way to the use of PANI-based materials
397 as substitutes for the presently employed activated carbon. This may lead to important economic
398 and environmental advantages related to the reusability of PANI1 and substitution of the hazardous
399 extraction solvent (carbon disulfide) with the less toxic methanol.

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