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# Surge of Green: Polyaniline-Based Materials for CO<sub>2</sub> Capture

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**Abstract:** Climate change driven by greenhouse gases emissions demands urgent action. Among the strategies currently investigated to curb greenhouse gases concentrations in the atmosphere, CO<sub>2</sub> adsorption and valorization are raising increasing interest. Polyaniline (PANI)-based materials have showed high affinity for CO<sub>2</sub>, due to their nitrogen content, and can thus be used as reversible adsorbents for CO<sub>2</sub> removal from gaseous effluents. Pristine PANI, PANI composites and PANI derived carbons have been recently investigated as alternative candidate to traditional materials. In this review, the properties of PANI and its main synthetic methods are briefly described, then an overview of the main classes of PANI-based materials used for CO<sub>2</sub> sorption and valorization is presented in order to stimulate further investigation that can contribute to widen the information on the unique properties of this polymer.

**Keywords:** polyaniline, N-rich carbons, composites, CO<sub>2</sub> capture, adsorption.

## 1. INTRODUCTION

The intense utilization of fossil fuels for energy production has led to a drastic increase in the CO<sub>2</sub> atmospheric emissions with negative repercussions on the planet. Among these, climate changes and the acidification of the oceans are the most evident effects of the negative consequences of the CO<sub>2</sub> levels in the Earth's atmosphere. The global average atmospheric concentration of CO<sub>2</sub> in 2019 was  $409.8 \pm 0.1$  ppm [1] and, if concrete actions are not implemented, this value will continue to growth inexorably. In the last decades, most developed countries have pursued policies aimed at reducing CO<sub>2</sub> and more in general Greenhouse Gas Emissions by at least 55% by 2030 [2].

Different approaches have been developed to lower CO<sub>2</sub> emissions: promoting energy conservation efficiency, replacing traditional energy sources with renewable ones (e.g., solar light, hydropower, wind energy, etc.), reforestation, using low carbon fuels (e.g., natural gas and nuclear power), geological sequestration, gas-separation membranes and mineralization/biomineralization, and CO<sub>2</sub> capture and storage [3-5]. Currently, these latter approaches represent attractive options to reduce atmospheric CO<sub>2</sub> levels by cheap processes [6-8].

For the removal of CO<sub>2</sub> from gas streams in industrial field absorption process by aqueous amine solutions have been extensively investigated. However, the costs of the process represent an important limit for real applications, along with additional drawbacks.

Even though good CO<sub>2</sub> uptake have been obtained by amine based ionic liquids, the demanding preparation process discourages further investigations [9-11].

In the last decades, the scientific community has addressed its efforts in the development of innovative materials and technologies for CO<sub>2</sub> capture. Among these, solid sorbents seem to offer interesting perspectives [12, 13]. In particular, carbon-based compounds show extraordinary performances thanks to their high chemical and physical stability, high surface area, pore-size tenability and ease surface functionalization [14-16].

Moreover, it has been demonstrated that the presence of basic sites on the sorbents surface enhances their CO<sub>2</sub> capture ability [17]. In fact, basic sites promote the interaction between the acidic CO<sub>2</sub> molecules and the carbon surface and N-doped activated carbons have been extensively investigated for this purpose [18-20]. However, the high cost of nanostructured carbons preparation limits their commercial use at large scale.

Polyaniline (PANI), as well as polypyrrole, is a nitrogen rich polymer extensively investigated for their versatility for several applications: sensors [21] biomedicine [22], conducting wires [23], etc. In addition, PANI-based materials find application as sorbents for the removal of different types of pollutants from air and water [24-27]. Despite the presence of amine groups should guarantee good performances for CO<sub>2</sub> chemisorption, PANI application in this field has received so far a limited attention. In this review, we offer an overview of the literature reports about the use of PANI and PANI-derived materials for CO<sub>2</sub> capture

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and valorization. Furthermore, we discuss the perspectives for the application of PANI-based material as adsorbents for CO<sub>2</sub> removal and catalysts for (photo)electrochemical reduction.

## 2. POLYANILINE: PROPERTIES AND SYNTHETIC METHODS

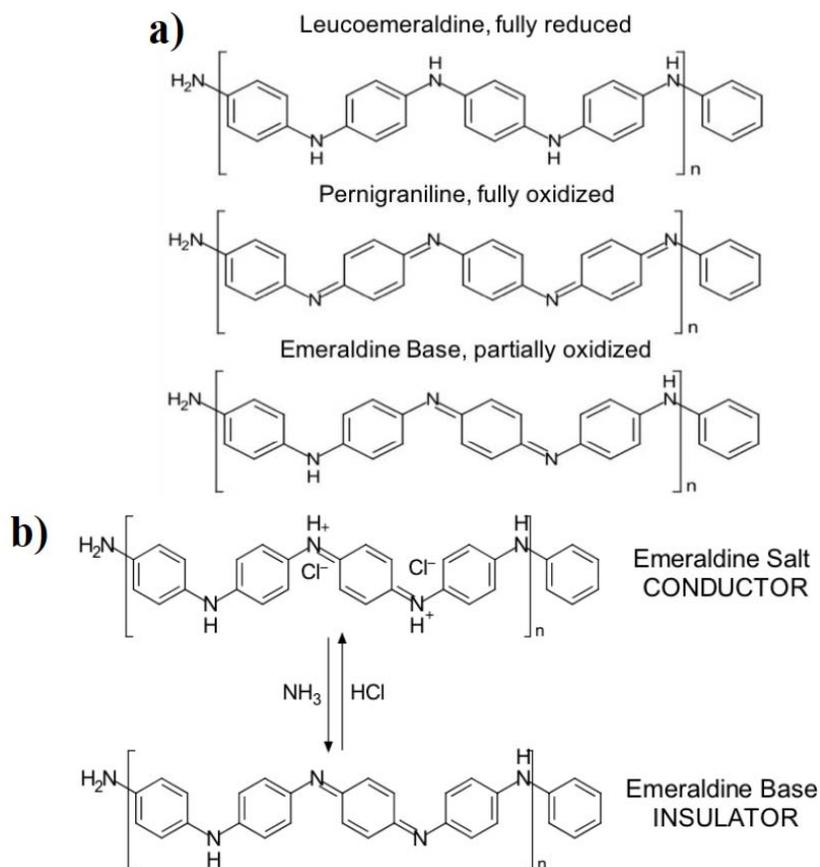
The PANI family is a class of polymers characterized by the presence of repeated aniline units connected to each other in the backbone. The nitrogen atom between the phenyl rings gives rise to different polymer oxidation states: the PANI physicochemical properties, such as its optical, structural and electrical features, are strictly related to its oxidation degree. Figure 1a reports the three main PANI structures which differ for the oxidation state: leucoemeraldine (the totally reduced form characterized by the presence of aminophenyl groups), pernigraniline (the totally oxidized form containing iminoquinone groups) and emeraldine (the half-oxidized form characterized by an alternation of aminophenyl and iminoquinone groups).

Beside these three main structures, many other intermediate forms exist, such as protoemeraldine,

which has an oxidation state intermediate between leucoemeraldine and emeraldine, and nigraniline, characterized by an oxidation degree between emeraldine and pernigraniline [28].

Furthermore, each form of polyaniline exists either as a base or as a protonated salt. Among all the possible polyaniline structures, only emeraldine in its protonated form (emeraldine salt, ES) exhibits conductive properties: the complete protonation of all the imine nitrogen atoms leads to the formation of delocalized polysemiquinone radical cations that increase the electronic conductivity of the polymer [28]. Thus, polyaniline, in its emeraldine form, is able to switch from an insulating state (emeraldine base, EB) to a conductive one (ES) through a simple pH variation (Figure 1b).

The versatile properties of polyaniline arising from its numerous oxidation and protonation states open the way to a wide spectrum of applications ranging from electronics and optics to photovoltaics [29, 30]. In recent years, PANI and its composites have been adopted as sorbents for environmental remediation both in water and air matrixes [24-27]. For its unique



**Figure 1:** a) The three main oxidation states of polyaniline; b) protonated (salt) and deprotonated (base) emeraldine forms.

properties, PANI is able to sorb a wide variety of pollutants, both organic and inorganic species, such as dyes, aromatic compounds, alcohols, metal ions, gas species, etc. [24-27, 31]. The intrinsic sorption capacity of PANI materials is related to the polymer ability to form different kinds of interactions with the pollutant: from electrostatic attraction and hydrogen bonding, to  $\pi$ - $\pi$  interactions and complexes formation. It is noteworthy, that PANI sorption-capacity is deeply influenced by its surface area that together with its pore volume and pore density influences the number of available sorption-sites. Another parameter to consider for the optimization of the PANI sorption capacity is the nature of the ES dopant, which plays an important role in the formation of interactions with the pollutant [31]. In this context, the synthetic procedure adopted for the PANI synthesis has a strong impact on the final material performances.

Over the years, even though a huge number of procedures have been developed for PANI synthesis, all these approaches are generally based on the oxidative polymerization of aniline. The majority of these methods can be gathered in two main categories: electrochemical and traditional chemical routes.

If on the one hand the electrochemical way is preferable for the synthesis of small amounts of polymer with high purity and control over morphology and conductivity, especially required for the preparation of thin conducting polymer films, e.g. in electrodes for sensing applications [28, 32], on the other hand the chemical oxidative polymerization approach represents the oldest and the most popular method to prepare polyaniline in large scale, although it does not enable a fine control over morphology and physicochemical properties of the polymer. Over the years, the effect of various experimental conditions on the quality of the material has been investigated: temperature, pH, reactant quantity and type of oxidant agent. Although this conventional approach represents a quick and easy procedure, it leads to several disadvantages, such as the noxious nature of the reagents (aniline, persulfates), the production of large amounts of inorganic co-products (sulfates) and organic by-products (benzidine and *trans*-azobenzene), which require additional purification step and, as consequence, produce large volumes of waste with a negative effect on the costs of the process. Alternative procedures, such as direct and inverse emulsion polymerization [33], interfacial polymerization [34], vapor-phase deposition polymerization [35],

sonochemical synthesis [36], etc. allow to obtain polymers with tailored properties.

The stringent environmental constrains and the increasing demand for highly pure materials in specific fields have contributed to the development of innovative catalytic approaches offering green ways towards PANI production [28]. In this regard, it was demonstrated that when the traditional stoichiometric oxidants are replaced by eco-friendlier oxidizing agents, such as H<sub>2</sub>O<sub>2</sub> or molecular oxygen, in the presence of proper catalysts only water is obtained as the reduction product [24-28, 31]. This result simplifies the post-treatment processes and reduces waste production. Cu, Pd, Au, Ag and Fe resulted valid catalysts for aniline polymerization. In order to replace toxic and carcinogenic aniline with alternative benign reagent, an aniline dimer (*N*-(4-aminophenyl aniline)) was proposed [37-39]. Furthermore, the use of *N*-(4-aminophenyl aniline) as avoid the production of toxic, carcinogenic and mutagenic by-products, such as benzidine and *trans*-azobenzene [25], further reducing the risk of exposure to hazardous compounds. However, this synthetic approach does allow a good control of the polymer growth. In fact, the high speed of the process leads to a PANI with compact morphology and low surface area and porosity.

In order to overcome this drawback, another eco-friendly approach has been proposed based on the photoinduced oxidative polymerization of aniline dimer that permits a good control over the reaction pathway [25]. The process is divided in two steps and involves the use of titanium dioxide as the photocatalyst and hydrogen peroxide as the oxidant. In the first step of the reaction, a UV-photoinduced growth of the oligomer chains occurs on the surface of titanium dioxide nanoparticles followed by the oligomers polymerization after the addition of hydrogen peroxide. By changing the photocatalysts and oxidant amounts, the polymer physicochemical properties can be tailored *ad hoc* [26].

### 3. PANI-BASED MATERIALS FOR CO<sub>2</sub> REMOVAL

Different types of PANI-based materials were investigated for CO<sub>2</sub> adsorption and valorization. While composites with carbon and inorganic porous materials, as well as carbonized PANI, have been used as effective CO<sub>2</sub> sorbents, pure and metal-modified PANI has been investigated for the electrochemical reduction of CO<sub>2</sub> to value-added chemicals. Table 1 compares literature reports about different classes of PANI-based CO<sub>2</sub> sorbents, while Table 2 summarizes

**Table 1: An Overview of the Main Literature Reports about PANI-Based Materials and Composites as CO<sub>2</sub> Adsorbents**

Type of material	Promoting material	Surface area (m <sup>2</sup> /g)	working conditions	CO <sub>2</sub> adsorption capacity (mmol/g)	CO <sub>2</sub> /N <sub>2</sub> selectivity (15% CO <sub>2</sub> and 85% N <sub>2</sub> mixture)	cyclability	Ref.
PANI composites with micro/mesoporous inorganic materials	APTES - functionalized silicone	-	308 K, 1.1 atm, 15% CO <sub>2</sub> /85% N <sub>2</sub> mixture	-	-	Recovery: 92.46 %; Purity: 47.65 %	40
	mesoporous silica, SBA-15	419 – 646	-	-	-	-	41
	octavinylsilsesquioxane	91 – 461	298 K, 1 bar	0.59	-	-	42
	MOF MIL-101(Cr)	631	298 K, 1 atm	2.6-3.9	4-14	6 cycles (desorption at 150°C in vacuum)	43
	MOF MIL-101(Cr)	631	273 K, 1.2 bar	2.26	Higher selectivity for CO <sub>2</sub>	-	44
	magnetite nanocapsules	-	301 K, 14.5 bar	54.21	-	-	45
PANI composites with carbon materials	graphene	-	298 K, 11 bar	75	-	20 cycles (re generation 140°C in vacuum)	46
	CNT	-	298 K, 11 bar	67	-	re generation at 140°C in vacuum	47
	activated carbon	554-736	298 K, 1 bar	2.69-3.16	6.91-18.97	-	48
	N-doped activated carbon	1297	298 K, 1 bar	3.96	47.17	-	49
	graphene oxide + Fe <sub>3</sub> O <sub>4</sub> , carbon nanofibers	<5 - 42	300 K, 1 bar	1.31-1.27	2 -21	5 cycles (333 K in N <sub>2</sub> flux)	50
carbonized PANI	hierarchically porous carbon from polymer hydrogel	1548-4196	298 K, p <sub>CO<sub>2</sub></sub> =30 bar	18.9-28.3	11.2-14.4 (mixture 10% CO <sub>2</sub> - 90% CH <sub>4</sub> )	10 cycles (isothermal desorption, 1 bar)	51
	KOH-activated carbon	1990-4240	273 K, 1 atm	4.4-7.6	-	-	20
	Microporous carbon	404-2994	273 K, p <sub>CO<sub>2</sub></sub> = 1 bar	4.00–6.85	8.12-8.42	3 cycles	52
	N-doped porous carbon	723	298 K, p <sub>CO<sub>2</sub></sub> = 1 bar	1.9	-	4 cycles	53
	N-enriched porous carbon from melamine-loaded PANI	432	298 K, 1 atm	1.8-4.6	25-110	5 cycles	54
	porous N functionalized graphene adsorbent	1336	273 K, 1 atm	5.8	17.9 (selectivity CO <sub>2</sub> /CH <sub>4</sub> = 4.3)	7 cycles (10% decrease in ads capacity)	55
	N-rich hierarchically porous carbon	309-2036	273 K, p <sub>CO<sub>2</sub></sub> = 1 bar	1.38-9.14	-	8 cycles (115°C vacuum degasing)	56
	N-doped porous carbon	567-1006	298 K, p <sub>CO<sub>2</sub></sub> = 1 bar	2.27-3.54	6.41-26.32	-	57

**Table 2: Summary of the Main Literature Studies on PANI-Based Materials as Catalysts for CO<sub>2</sub> (Photo) Electrochemical Reduction**

Catalyst	Process	Working potential	Cell type	Supporting electrolyte	irradiation	reduction products	Faradaic Efficiency	Ref.
polyaniline electrode	Electrochemical reduction	-0.4 V vs. SCE	three electrode, Nafion 417 membrane cell at ambient conditions	0.25 M LiClO <sub>4</sub> /methanol	-	formic acid and acetic acid	12% for formic acid and 78% for acetic acid	58
Polyaniline film	Photoelectrochemical reduction	-0.41 V vs. Ag/AgCl/3 M NaCl	sealed two-compartment photoelectrochemical cell	0.1 M NaHCO <sub>3</sub> saturated with CO <sub>2</sub> (pH = 7)	UV-vis light irradiation (100 W)	methanol and ethanol	methanol 43%, ethanol 20%, H <sub>2</sub> 20%	59
PANI-CNT + Pd	Electrochemical reduction	-0.8 V vs. SCE	3-electrode electrochemical cell equipped with a luggin capillary and Nafion 211 membrane, working at RT and p atm	0.1 M KHCO <sub>3</sub> saturated with CO <sub>2</sub>	-	formic acid	83%	60
Sn-doped PANI film on Ni foam	Electrochemical reduction	-1.14 V vs. RHE	three-electrode, undivided cell	0.1 M KHCO <sub>3</sub> saturated with CO <sub>2</sub>	-	formate	94%	61
Gold-PANI Core-Shell Nanocomposite	Electrochemical reduction	-0.9 V vs. RHE	gas-tight two-compartment, three electrode glass H-cell separated by a Nafion membrane	0.1 M KHCO <sub>3</sub> saturated with CO <sub>2</sub> (pH = 6.8)	-	CO	85%	62
PANI film on Cu electrode and Cu NPs	Electrochemical reduction	-1.1 V vs. RHE	H-type electrolytic cell equipped with three electrodes and separated by an anion exchange membrane, quaternary ammonia poly(N-methylpiperidine-co-p-terphenyl)	0.1 M KHCO <sub>3</sub> saturated with CO <sub>2</sub> (pH = 6.8)	-	hydrocarbon products, e.g., methane, ethylene, and ethanol	60% for the film, 80% for the coated NPs	63

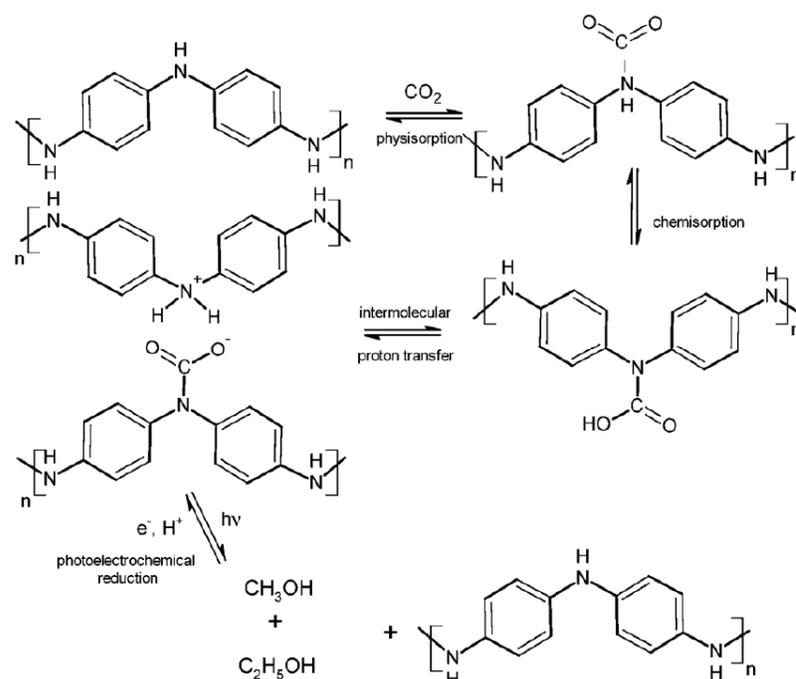
studies on PANI-based materials used for CO<sub>2</sub> reduction.

### 3.1. Pristine and Metal-Modified PANI

Despite PANI promising properties in terms of CO<sub>2</sub> sorption and reduction, only few works focus on the application of pristine polyaniline in this field. In this regard, Rebattet *et al.* [64] studied the sorption of different gasses, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>, on PANI powders and films with different degree of HCl doping. They found that, in undoped samples, CO<sub>2</sub> was

adsorbed ten times more than O<sub>2</sub> and N<sub>2</sub>, while in the doped samples, the CO<sub>2</sub> / O<sub>2</sub> or N<sub>2</sub> ratio was closed to twenty. For all samples the CO<sub>2</sub>/CH<sub>4</sub> sorption ratio was equal to five. These findings showed that the selectivity of PANI towards CO<sub>2</sub> adsorption increases with the polyaniline doping level and that the adsorption isotherm of CO<sub>2</sub> follows a Langmuir model.

Large part of the scientific literature reports the use of pristine and metal-modified PANI for CO<sub>2</sub> sorption coupled with its(photo)electrochemical reduction to organic compounds or CO. In these regards, Hursán *et*



**Scheme 1:** Possible mechanistic pathway for CO<sub>2</sub> adsorption and photoelectrochemical reduction on PANI. Reproduced from Ref [59]. with permission from the Royal Society of Chemistry.

*al.* [59] applied polyaniline as photocathode material for the sorption and conversion of CO<sub>2</sub> to alcohol fuels. The study highlights the presence of a specific chemical interaction between PANI and CO<sub>2</sub> molecules, which results in the formation of carbamic acid and carbamate (Scheme 1).

For CO<sub>2</sub> photoreduction the band edge positions of the polymer are critical: in polyaniline the conduction band edge is negative enough for the photogenerated electrons to reduce CO<sub>2</sub> and the valence band edge is positive enough to make the conducting polymer behave as a semiconductor (rather than as a semi-metal) at the applied electrical potential [59]. It is noteworthy that no co-catalyst was needed for sustaining the photoconversion of CO<sub>2</sub> to alcohol products.

Köleli *et al.* proposed several studies [58, 65] based on the electrochemical reduction of CO<sub>2</sub> with a PANI-coated electrode by using methanol as a solvent and generating formic acid and acetic acid as reaction products. The optimum film thickness was found to be 0.6 mm: with thicker PANI films, crumbling of the coating was observed, while thinner films had a lower current density and a smaller active surface. The adsorption of CO<sub>2</sub> on PANI is a fundamental step for the molecule reduction: when H<sup>+</sup> ions are adsorbed at the PANI surface (H<sub>ad</sub>), they are added to the adsorbed CO<sub>2</sub> and produce HCOO<sub>ad</sub>, which recombine with

further H<sub>ad</sub> to give formic acid. HCOO<sub>ad</sub> species can also be subjected to the attack of a solvent molecule (CH<sub>3</sub>OH), generating acetic acid. More recently, Köleli *et al.* [58] investigated CO<sub>2</sub> reduction on PANI electrodes at -0.4 V<sub>SCE</sub> in a Nafion 417 membrane cell at ambient conditions: the maximum Faradaic efficiencies were found to be 12% for formic acid and 78% for acetic acid.

Some very recently works [61-63] focused on PANI-metal electroactive composites by the deposition or polymerization of PANI on gold, copper or nickel. In all cases, the ability of PANI to adsorb CO<sub>2</sub> was essential in order to increase the reduction Faradic efficiency. Vijayakumar *et al.* [62] worked on shape-tailored gold-PANI nanocomposite electrocatalysts which exhibited a core-shell structure with gold as the core and PANI as the shell. The interaction between Au nanoparticles and amine links in PANI through  $\sigma$ -electron donation facilitates CO<sub>2</sub> adsorption and stabilizes COOH<sub>ad</sub> intermediate, thus promoting the reduction of CO<sub>2</sub> to CO, reaching a conversion efficiency of 85% with a current density of 11.6 mA cm<sup>-2</sup>. Wei *et al.* coated a thin PANI film on a Cu electrode [63] in order to enhance the C<sup>2+</sup> selectivity of polycrystalline copper toward the electrochemical reduction of CO<sub>2</sub>. Upon coating with PANI, the hydrogen evolution side reaction on Cu was suppressed to some degree, the current density of the CO<sub>2</sub> reduction was thus increased and, more importantly, the C<sup>2+</sup> hydrocarbons became the

major product. This effect was ascribable to a synergy of the Cu/PANI interface. With a 50 nm thick PANI film, the Faradaic efficiency reached 60% at  $-1.1 V_{RHE}$  in KHCO<sub>3</sub> solutions and when PANI was coated onto Cu nanoparticles, the Faradaic efficiency of C<sup>2+</sup> hydrocarbons could even reach 80%. Li [61] proposed a Sn-doped PANI-nickel foam composite, obtained from aniline polymerized on a Ni foam electrode: PANI nanowires grew with wire diameters of approximately 150 nm to cover the entire electrode surface and then metal Sn was deposited on the composite. Compared with the Sn-nickel foam electrode, the Sn@PANI-nickel foam (doped with methanesulfonic acid) electrode showed superior activity towards the electrochemical reduction of CO<sub>2</sub> to formate, for the excellent PANI ability to adsorb CO<sub>2</sub>. The maximum Faradaic efficiency was 94% with a space time yield of 306 mmol h<sup>-1</sup> cm<sup>-2</sup> at the electrolytic potential of 1.70 V.

### 3.2. Composites of PANI with Micro-and Mesoporous Inorganic Materials

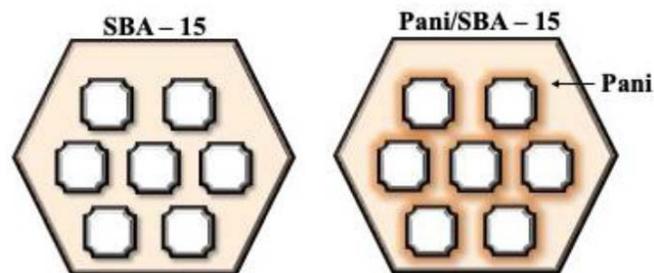
Siliceous materials have drawn the attention as supports for CO<sub>2</sub> sorbents due to their ordered porous structure and distribution, or to their amorphous character, high surface area and ability to be modified by amine-based molecules.

Yang *et al.* [40] studied the adsorption properties of a silicon based material (3-aminopropyltriethoxysilanes) modified with polyaniline. They performed Temperature Swing Adsorption (TSA) experiments evaluating different operative variables. They obtained an optimum adsorption temperature of 308 K, a desorption temperature of 383 K, a feed pressure of 1.10 atm, and a CO<sub>2</sub> purity of 47.65% with a recovery of 92.46%.

The same material was tested by Chou *et al.* [66] to assess the best type of adsorption process among single-bed five-step TSA, single-bed two-step PSA (Pressure Swing Adsorption), single-bed three-step PSA, and dual-bed six-step PSA. Results demonstrated that the best adsorption process was the single-bed three-step PSA, operating with a feed pressure of 6 atm, obtaining 97.13% of purity and 87.26% of CO<sub>2</sub> recovery.

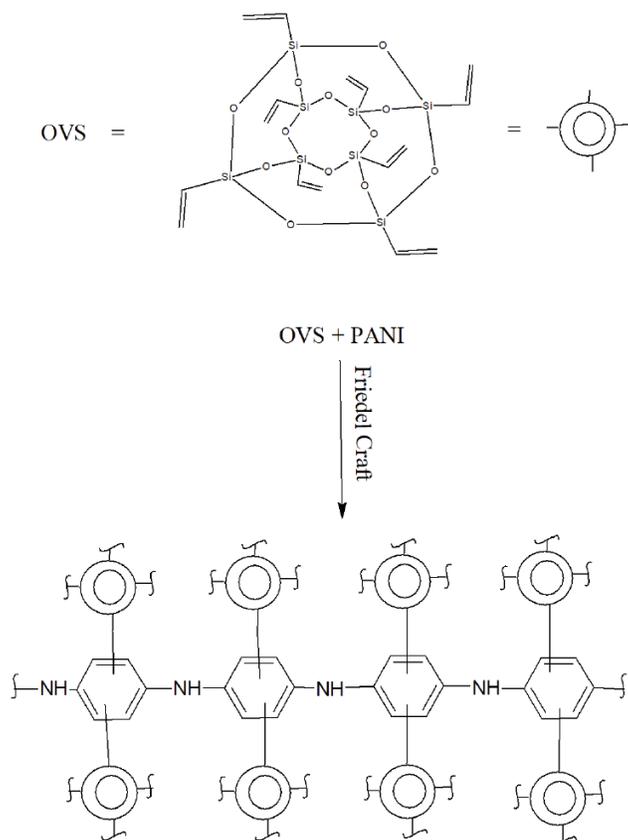
Boukoussa *et al.* [41] prepared PANI/SBA-15 nanocomposite through *in situ* polymerization of aniline (Figure 2). The presence of amino groups on the thin-film of polyaniline improves the chemisorption and physisorption of CO<sub>2</sub> when polyaniline content is raised up to 30%. Moreover, they found out that a higher

content of polyaniline could obstruct the pores of SBA-15 material leading to the formation of aggregates and clusters.



**Figure 2:** Schematic representation of thin layers of Pani in the inner surface of SBA-15.

An hybrid porous hypercrosslinked polyaniline was synthesized through Friedel-Craft reaction with octavinylsilsequioxane (OVS) by Tang *et al.* [42] (Figure 3).



**Figure 3:** Synthetic routes of OVS-pani composites.

Controlling the mass ratio of OVS to polyaniline it was possible to reach a CO<sub>2</sub> uptake capacity of 0.59 mmol g<sup>-1</sup> (2.60 wt%) at 298 K and 1.01 bar.

Metal Organic Frameworks (MOFs) have been proposed for this kind of applications. They are

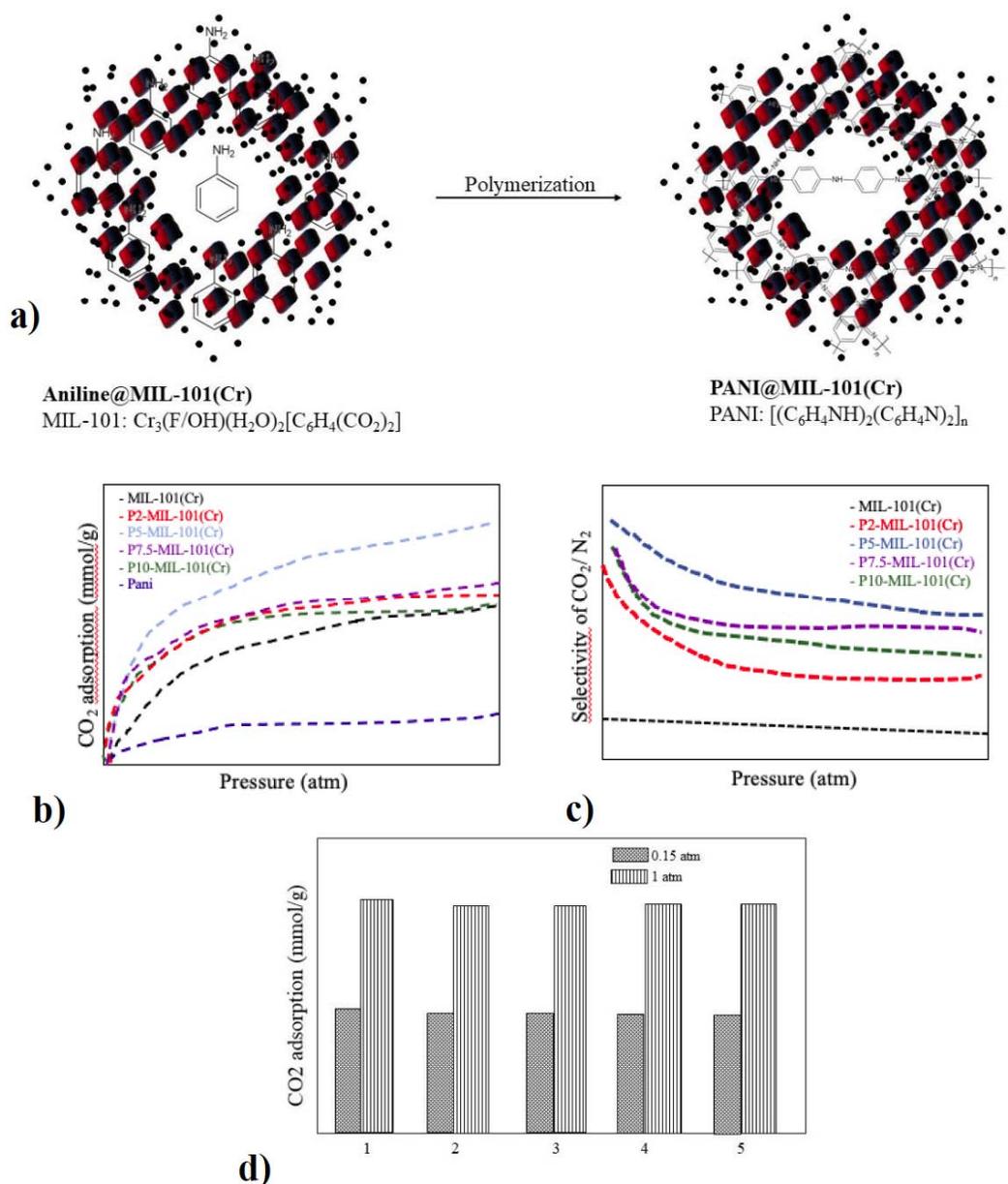
crystalline materials constituted by metal ions coordinated to organic ligands to form ordered structures with high porosity and high surface area. The surface properties of these materials can be tuned by organic ligand variations to improve the adsorption performances towards CO<sub>2</sub>.

Yoo et al. [43] have successfully prepared a highly porous MOF MIL-101(Cr) modified with PANI through *in situ* polymerization of aniline (Figure 4a).

They verified that the presence of amino groups of PANI on the material surface could effectively improve

the adsorption capacity (3.9 mmol/g at 1 atm (Figure 4b) and selectivity towards CO<sub>2</sub> (CO<sub>2</sub>/N<sub>2</sub> = 14 (Figure 4c). Furthermore, the results confirmed the reusability of the materials up to five adsorption/desorption cycles (Figure 4d).

A similar hybrid material was synthesized by Aliev et al. [44] using *intra*-channel polymerization of aniline on metal organic framework MIL-101(Cr). The composite demonstrated an adsorption capacity of CO<sub>2</sub> of 2.26 mmol g<sup>-1</sup> at 273K. Moreover, the introduction of N-rich groups on MOF surface has led to a higher selectivity to CO<sub>2</sub> over N<sub>2</sub>.



**Figure 4:** a) Schematic procedure for PANI@MIL-101(Cr) production from aniline-loaded MIL-101(Cr) through *in-situ* polymerization; b) CO<sub>2</sub> adsorption isotherms over MIL-101(Cr) and PANI at 273 K; c) Selectivity for CO<sub>2</sub>/N<sub>2</sub> (0.15/0.75) over MIL-101(Cr) at 288 K. d) Reusability of PANI/MIL-101(Cr) for CO<sub>2</sub> adsorption at 298 K under pressure of 0.15 or 1 atm.

Metal oxides have drawn great interest in CO<sub>2</sub> adsorption capacity due to the formation of carbonates, bicarbonates, and carboxylates. Specifically, nanostructured magnetite has revealed high adsorption capacity as a result of its high surface area, well-defined porous structure and great affinity towards CO<sub>2</sub>. Tamilarasan *et al.* [45] developed polyaniline/magnetite nanocapsules (PANI/MNCs) which have shown 54.21 mmol g<sup>-1</sup> of adsorption capacity at 14.5 bar and 301 K in response to physical and chemical interaction with CO<sub>2</sub> molecules. Additionally, they observed no activity loss on the same material even after 15 recycles at different pressure and temperatures.

### 3.4. Composites of PANI with Carbon-Based Materials

Thanks to their extraordinary chemical-physical characteristics, such as large surface area, high and tunable porosity, ease surface functionalization and wide availability, carbon-based materials (activated carbon, carbon nanotubes, carbon nanofibers, carbon nanospheres, etc.) represent promising adsorbents for CO<sub>2</sub> capture [67-70]. However, the high costs of production and activation of these materials generally limit their real applications.

However, it has been demonstrated that proper surface modifications can enhance their stability and CO<sub>2</sub> sorption capability, offering these materials a new chance.

In particular, the development of nitrogen-doped carbons from PANI and PANI/carbon composites have opened a new era for this kind of materials. In fact, the high surface area and porosity, the good mechanical strength and the hydrothermal stability of carbons combined with the good affinity of the amine groups of PANI towards CO<sub>2</sub> make this new generation of sorbents very promising for applications in different real conditions.

Mishra and Ramaprabhu reported the extraordinary increase in CO<sub>2</sub> adsorption capacity of both graphene sheets and multiwalled carbon nanotubes when decorated with PANI (PANI-f-HEG and PANI-f-MWNTs respectively) [46, 47]. The sorption tests, carried out at different temperatures (25, 50 and 100°C) and at 11 bar, demonstrating the good CO<sub>2</sub> uptake of these materials are reported in Figure 5).

PANI-f-HEG reaches a CO<sub>2</sub> adsorption capacity of 75 mmol/g (25°C), 50 mmol/g (50°C) and 25 mmol/g

(100°C) at 11 bar, about 30% higher than the results obtained for pristine graphene (21.6, 18 and 12 mmol/g at the same temperatures). At the same conditions similar results were obtained for PANI-f-MWNTs, reaching a CO<sub>2</sub> uptake of 67 mmol/g, 46 mmol/g and 27 mmol/g, about 37% higher than pristine MWNTs.

The tests show that CO<sub>2</sub> capture capacity of PANI-f-HEG decreases with increase in temperature and increases with increase in the pressure. The positive effect of the pressure increase on the CO<sub>2</sub> uptake is related to multilayer gas adsorption processes through the nitrogen containing groups and to the large availability of CO<sub>2</sub> molecules when the pressure increases. On the other hand, the negative effect of the temperature increase can be attributed to the higher kinetic energy of gas molecules at high temperatures that lead to desorption phenomena.

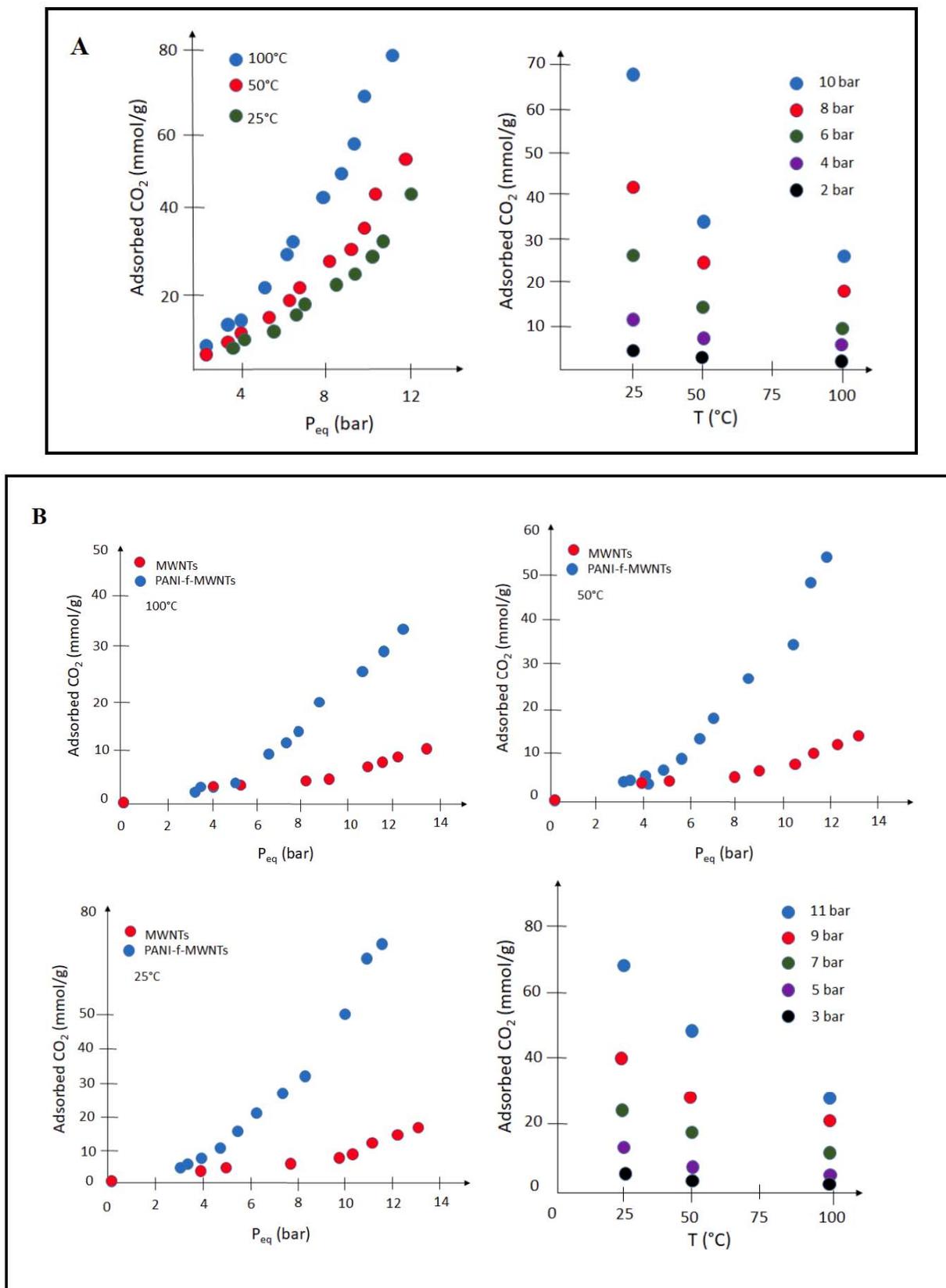
A possible mechanism of CO<sub>2</sub> uptake on the nitrogen groups of the composite is proposed and consists on chemical interactions between the gas molecules and the N-rich groups of the material, followed by the formation of bidentate carbonates and carbamates, as confirmed by FT-IR spectroscopic investigations.

Subjected to consecutive sorption/desorption (high temperature treatment) cycles, the composite maintained constant performances demonstrating the possibility to be easily reused for many cycles.

Advanced PANI-modified carbon nanofibers (AC/PANI/F) and nanospheres (AC/PANI/S) were recently synthesized by Khalili *et al.* [48]. If compared to the previous results, the adsorption ability of these materials are modest even if higher than the corresponding pristine activated carbon. AC/PANI/F and AC/PANI/S reached a CO<sub>2</sub> uptake of 2.69 mmol/g and 3.16 mmol/g at 25°C and 1 bar, about three times the value of the corresponding pristine activated carbon in the same conditions (1.19 mmol/g). On the contrary of the modest results in terms of CO<sub>2</sub> adsorption, the composites showed extraordinary results in terms of selectivity, leading to values of 18.69 and 6.1 respectively for AC/PANI/F and AC/PANI/S respectively (selectivity of pristine AC = 1.53). The very promising result obtained for the modified nanofibers are related to a higher load of PANI on the surface.

### 3.5. PANI-Derived Porous Carbons

PANI materials can be also used to obtain N-rich carbon materials with extremely high surface area and



**Figure 5:** CO<sub>2</sub> adsorption isotherms and CO<sub>2</sub> adsorption dependence from temperature for: **A)** PANI-f-MWNTs; **B)** PANI-f-MWNTs.

surface porosity, by controlled carbonization at temperatures in the 400-800°C range [20]. Due to their

N content, which promotes polarity and surface basicity, and high porosity, these materials are

extremely promising candidates for CO<sub>2</sub> adsorption, showing high adsorption capacities [51]. To further increase the N-content, Park *et al.* [54] recently reported the use of melamine-loaded PANI as starting material.

In order to promote the absorption properties of the obtained carbon, an activation post-treatment is generally performed. Different types of activating agents can be used, such as KOH [20,51, 57, 71], and ZnCl<sub>2</sub> [57].

The use of PANI hydrogels as starting materials can result in products with extremely high surface area (over 4000 m<sup>2</sup>/g) and porosity (> 2 cm<sup>3</sup>/g) [51]. However, it has been consistently reported that the narrow porosity, rather than the surface area and even of the total porosity, is the main controlling factor in determining the CO<sub>2</sub> adsorption capacity of activated carbons [20, 54,56, 57,71]. For instance, Qezelsefloo *et al.* reported a higher CO<sub>2</sub> adsorption capacity by a ZnCl<sub>2</sub>-activated sample carbonized at 500°C with respect to a sample characterized by a surface area over 60% larger and by a more than doubled total pore size (3.54 vs. 2.59 mmol/g) [57]: they attributed the enhanced performance to the smaller pore diameter and higher nitrogen content of the ZnCl<sub>2</sub>-activated sample. These experimental observations have been also supported by molecular simulations showing an increased density of adsorbed CO<sub>2</sub> in micro- and narrow mesopores at high pressures [51].

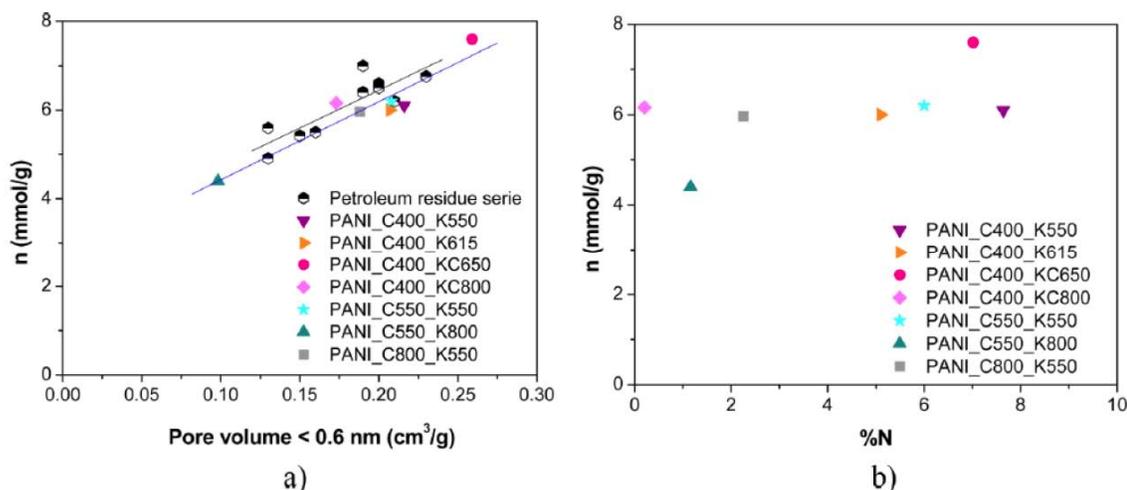
The narrow microporosity has been reported to play a more important role even than N content [20]. Figure 6 reports correlation graphs between the CO<sub>2</sub>

adsorption capacity of activated carbon materials as a function of narrow micropores volume and N content. A linear dependence of the CO<sub>2</sub> uptake on the narrow microporosity is clearly appreciable, while data about N content are more scattered.

It has been proposed that a critical pore size in CO<sub>2</sub> adsorption can be identified [71]: micropores with a diameter smaller than the critical value play a determine role on the CO<sub>2</sub> adsorption capacity. Zhang *et al.* [71] suggested a dependence of this critical value on the adsorption pressure and temperature, with higher sorption temperatures (and lower pressures) requiring smaller pore sizes. They reported that pores smaller than 0.54 nm were controlling the CO<sub>2</sub> capture capacity for sorption at 75 °C. Other authors reported critical values at 0°C and atmospheric pressure of 0.6 nm [20] and of 0.7 nm [56].

The pore size distribution can be tailored by varying the carbonization temperature. [51]. For PANI-derived carbon activated with KOH, Silvestre-Albero *et al.* reported that carbonization temperatures in the 400–650 °C range yielded materials with a highly degree of micro- and mesoporosity, while high temperatures (up to 800 °C) led to microporous carbons [20]. MawunyaKutorglo *et al.* [56] developed activated carbons with a hierarchical pore structure from PANI prepared by a template synthesis using polystyrene sphere: the hierarchical pore structure enhanced the diffusion of CO<sub>2</sub> into the inner micropores.

It should be noted that, while the CO<sub>2</sub> capture capacity at low pressure is primarily controlled by the



**Figure 7:** Correlation between CO<sub>2</sub> adsorption (atmospheric pressure and 273 K) of porous carbon derived from PANI and from a petroleum residue with: **a)** volume of narrow micropores (< 0.6 nm); **b)** N content. eprinted (adapted) with permission from [20]. Copyright 2014 American Chemical Society.

presence of micropores, it is important to tune both the pore size distribution and surface chemistry (N content) simultaneously to combine their advantages [56].

#### 4. CONCLUSIONS

The present work summarized an overview of research studies on the PANI and PANI derivatives ability to capture CO<sub>2</sub>, demonstrating the extraordinary properties of this unique polymer in this field. In this respect, PANI composites with carbon allotropes as well as with inorganic micro/mesoporous materials have shown promising results, along with N-rich and highly microporous activated carbons. Despite the promising results the interest in this kind of materials for this application still seems modest. The advancement of knowledge in the development on processable PANI-based materials and the possibility of fabricate innovative products alternative to traditional powders have not yet been taken into consideration.

In this regards foams and membranes of PANI and its derivatives could represent interesting materials to face this global concern that invites everyone to contribute with their knowledge and efforts.

#### REFERENCES

- [1] Climate.gov science&information for a climate-smart nation. Lindsey, R: Climate Change: Atmospheric Carbon Dioxide. [Updated October 7, 2021; Published August 14, 2020]: Available from: <https://www.climate.gov/news-features/understanding-climate/climate-change-atmospheric-carbon-dioxide>
- [2] EUROPEAN COMMISSION. CLIMATE ACTION. Available from: [https://ec.europa.eu/clima/policies/eu-climate-action/2030\\_ctp\\_en](https://ec.europa.eu/clima/policies/eu-climate-action/2030_ctp_en)
- [3] Valkering P. Carbon capture and storage. In: IOP Conference Series: Earth and Environmental Science, 6, 2009, p. 392008. <https://doi.org/10.1088/1755-1307/6/3/392008>
- [4] MacDowell N, Florin N, Buchard A, Hallett J, Galindo A, Jackson G, Adjiman CS, Williams CK, Shah N, Fennell P. An overview of CO<sub>2</sub> capture technologies, *Energy Environ Sci* 2010; 3: 1645–69. <https://doi.org/10.1039/c004106h>
- [5] Boot-Handford ME, Abanades JC, Anthony EJ, Blunt MJ, Brandani S, Mac Dowell N, Fernández JR, Ferrari MC, Gross R, Hallett JP, Haszeldine RS, Heptonstall P, Lyngfelt A, Makuch Z, Mangano E, Porter RTJ, Pourkashanian M, Rochelle GT, Shah N, Yao JG, Fennell PS. Carbon capture and storage update, *Energy Environ Sci* 2014; 7: 130–89. <https://doi.org/10.1039/C3EE42350F>
- [6] Dzubak AL, Lin LC, Kim J, Swisher JA, Poloni R, Maximoff SN, Smit B, Gagliardi L. Ab initio carbon capture in open-site metal–organic frameworks, *Nat Chem* 2012; 4: 810-6. <https://doi.org/10.1038/nchem.1432>
- [7] Varghese A, Mittal V. Performance of Various Adsorbents Towards Diverse Gases: a Comparative Study, *Functional Nanomaterials and Nanotechnologies: Applications for Energy & Environment*. Central West Publishing, 2018; 305–404. <https://doi.org/10.1016/j.cej.2020.124022>
- [8] Varghese AM, Reddy KSK, Singh S, Karanikolos GN. Performance enhancement of CO<sub>2</sub> capture adsorbents by UV treatment: the case of self-supported graphene oxide foam, *Chem Eng J* 2020; 124022(1-11).
- [9] Baltus RE, Counce RM, Culbertson BH, Luo H, DePaoli DW, Dai S, Duckworth DC. Examination of the Potential of Ionic Liquids for Gas Separations, *Sep Sci Technol* 2005; 40: 525-41. <https://doi.org/10.1081/SS-200042513>
- [10] Huang J, Ruther T. Why are Ionic Liquids Attractive for CO<sub>2</sub> Absorption? An Overview, *Aust J Chem* 2009; 62: 298-308. <https://doi.org/10.1071/CH08559>
- [11] Gurkan B, Goodrich BF, Mindrup EM, Ficke LE, Massel M, Seo S, Senftle TP, Wu H, Glaser MF, Shah JK, Maginn EJ, Brennecke JF, Schneider WF. Molecular Design of High Capacity, Low Viscosity, Chemically Tunable Ionic Liquids for CO<sub>2</sub> Capture, *J Phys Chem Lett* 2010; 1: 3494-99. <https://doi.org/10.1021/jz101533k>
- [12] Wang QA, Luo JZ, Zhong ZY, Borgna A, CO<sub>2</sub> capture by solid adsorbents and their applications: current status and new trends, *Energy Environ. Sci* 2011; 4: 42-55. <https://doi.org/10.1039/C0EE00064G>
- [13] Wang JY, Huang L, Yang RY, Zhang Z, Wu JW, Gao YS, Wang Q, O'Hare D, Zhong ZY. Recent advances in solid sorbents for CO<sub>2</sub> capture and new development trends, *Energy Environ Sci* 2014; 7: 3478-3518. <https://doi.org/10.1039/C4EE01647E>
- [14] To JWF, Chen Z, Yao H, He J, Kim K, Chou HH, Pan L, Wilcox J, Cui Y, Bao Z. Ultrahigh Surface Area Three-Dimensional Porous Graphitic Carbon from Conjugated Polymeric Molecular Framework, *ACS Cent Sci* 2015; 1: 68-76. <https://doi.org/10.1021/acscentsci.5b00149>
- [15] Klett J, Hardy R, Romine E, Walls C, Burchell T. High-thermal-conductivity, mesophase-pitch-derived carbon foams: effect of precursor on structure and properties, *Carbon* 2000; 38: 953-73. [https://doi.org/10.1016/S0008-6223\(99\)00190-6](https://doi.org/10.1016/S0008-6223(99)00190-6)
- [16] Wu ZX, Zhao DY. Ordered mesoporous materials as adsorbents, *Chem Commun* 2011; 47: 3332-8. <https://doi.org/10.1039/c0cc04909c>
- [17] Zhang Z, Xu M, Wang H, Li Z. Enhancement of CO<sub>2</sub> adsorption on high surface area activated carbon modified by N<sub>2</sub>, H<sub>2</sub> and ammonia, *Chem Eng J* 2010; 160: 571-7. <https://doi.org/10.1016/j.cej.2010.03.070>
- [18] Casco ME, Martínez-Escandell M, Silvestre-Albero J, Rodríguez-Reinoso F. Effect of the porous structure in carbon materials for CO<sub>2</sub> capture at atmospheric and high-pressure, *Carbon* 2014; 67: 230-2. <https://doi.org/10.1016/j.carbon.2013.09.086>
- [19] Choma J, Jedynek K, Fahrenholz W, Ludwinowicz J, Jaroniec M. Microporosity development in phenolic resin-based mesoporous carbons for enhancing CO<sub>2</sub> adsorption at ambient conditions, *Appl Surf Sci* 2014; 289: 592-600. <https://doi.org/10.1016/j.apsusc.2013.11.051>
- [20] Silvestre-Albero A, Silvestre-Albero J, Martínez-Escandell M, Rodríguez-Reinoso F. Micro/Mesoporous Activated Carbons Derived from Polyaniline: Promising Candidates for CO<sub>2</sub> Adsorption, *Ind Eng Chem Res* 2014; 53: 15398-405. <https://doi.org/10.1021/ie5013129>
- [21] Sen T, Mishra S, Shimpi NG. Synthesis and sensing applications of polyaniline nanocomposites: a review, *RSC Adv* 2016; 6: 42196-222. <https://doi.org/10.1039/C6RA03049A>
- [22] Zare EN, Makvandi P, Ashtari B, Rossi F, Motahari A, Perale G. Progress in Conductive Polyaniline-Based Nanocomposites for Biomedical Applications: A Review, *J Med Chem* 2020; 9(63): 1-22. <https://doi.org/10.1021/acs.jmedchem.9b00803>

- [23] Song E, Choi JW. Conducting Polyaniline Nanowire and Its Applications in Chemiresistive Sensing, *Nanomaterials* 2013; 3(3): 498–523.  
<https://doi.org/10.3390/nano3030498>
- [24] Della Pina C, De Gregorio MA, Clerici L, Dellavedova P, Falletta E. Polyaniline (PANI): an innovative support for sampling and removal of VOCs in air matrices, *J Hazard Mater* 2018; 344: 1-8.  
<https://doi.org/10.1016/j.jhazmat.2017.10.012>
- [25] Cionti C, Della Pina C, Meroni D, Falletta E, Ardizzone S. Triply green polyaniline: UV irradiation-induced synthesis of highly porous PANI/TiO<sub>2</sub> composite and its application in dye removal, *Chem Comm* 2018; 54: 10702-05.  
<https://doi.org/10.1039/C8CC04745F>
- [26] Cionti C, Della Pina C, Meroni D, Falletta E, Ardizzone S. Photocatalytic and oxidative synthetic pathways for highly efficient PANI-TiO<sub>2</sub> nanocomposites as organic and inorganic pollutant sorbents, *Nanomaterials* 2020; 10(441): 1-21.  
<https://doi.org/10.3390/nano10030441>
- [27] Della Pina C, De Gregorio MA, Dellavedova P, Falletta E. Polyanilines as new sorbents for hydrocarbons removal from aqueous solutions, *Materials* 2020; 13: 2161(1-10).  
<https://doi.org/10.3390/ma13092161>
- [28] Della Pina C, Falletta E, Polyaniline: From Tradition to Innovation; Science, N., Ed.; 2015; ISBN 978-1-63463-273-7.
- [29] Baker CO, Huang X, Nelson W, Kaner RB. Polyaniline nanofibers: broadening applications for conducting polymers, *Chem Soc Rev* 2017; 46: 1510-25.  
<https://doi.org/10.1039/C6CS00555A>
- [30] Zhang J, Zhao Z, Xia Z, Dai L. A metal-free bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions, *Nat Nanotechnol* 2015; 10: 444-52.  
<https://doi.org/10.1038/nnano.2015.48>
- [31] Bianchi CL, Djellabi R, Della Pina C, Falletta E. Doped-polyaniline based sorbents for the simultaneous removal of heavy metals and dyes from water: unravelling the role of synthesis method and doping agent, *Chemosphere* 2022; 286; 141941(1-10).  
<https://doi.org/10.1016/j.chemosphere.2021.131941>
- [32] Lacroix JC, Camalet JL, Aeiayach S, Chane-Ching K, Petitjean J, Chauveau E, Lacaze PC. Aniline electropolymerization on mild steel and zinc in a two-step process, *J Electroanal Chem* 2000; 481: 76–81.  
[https://doi.org/10.1016/S0022-0728\(99\)00490-8](https://doi.org/10.1016/S0022-0728(99)00490-8)
- [33] Wei Z, Wan M. Hollow Microspheres of Polyaniline Synthesized with an Aniline Emulsion Template, *Adv Mater* 2002; 14: 1314-17.  
[https://doi.org/10.1002/1521-4095\(20020916\)14:18<1314::AID-ADMA1314>3.0.CO;2-9](https://doi.org/10.1002/1521-4095(20020916)14:18<1314::AID-ADMA1314>3.0.CO;2-9)
- [34] Huang J, Kaner RB. A General Chemical Route to Polyaniline Nanofibers, *J Am Chem Soc* 2004; 126: 851-5.  
<https://doi.org/10.1021/ja0371754>
- [35] Bhadra S, Lee JH. Synthesis of higher soluble nanostructured polyaniline by vapor-phase polymerization and determination of its crystal structure, *J Appl Polym Sci* 2009; 114: 331-40.  
<https://doi.org/10.1002/app.30524>
- [36] Jing X, Wang Y, Wu D, She L, Guo Y. Polyaniline nanofibers prepared with ultrasonic irradiation, *J Polym Sci Part A Polym Chem* 2006; 44: 1014-9.  
<https://doi.org/10.1002/pola.21217>
- [37] Chen Z, Della Pina C, Falletta E, Rossi M. A green route to conducting polyaniline by copper catalysis, *J Catal* 2009; 267: 93-6.  
<https://doi.org/10.1016/j.jcat.2009.07.007>
- [38] Dias HVR, Wang X, Rajapakse RMG, Elsenbaumer RL. A mild, copper catalyzed route to conducting polyaniline, *Chem Comm* 2006: 976-8.  
<https://doi.org/10.1039/b513938d>
- [39] Della Pina C, Ferretti AM, Ponti A, Falletta E. A green approach to magnetically-hard electrically-conducting polyaniline/CoFe<sub>2</sub>O<sub>4</sub> nanocomposites, *Compos Sci Technol* 2015; 110: 138-44.  
<https://doi.org/10.1016/j.compscitech.2015.02.007>
- [40] Yang MW, Chen NC, Huang CH, Shen YT, Yang HS, Chou CT. Temperature swing adsorption process for CO<sub>2</sub> capture using polyaniline solid sorbent, *Energy Procedia* 2014; 63: 2351-8.  
<https://doi.org/10.1016/j.egypro.2014.11.256>
- [41] Boukoussa B, Hakiki A, Nunes-Beltrao AP, Hamacha R, Azzouz A. Assessment of the intrinsic interactions of nanocomposite polyaniline/SBA-15 with carbon dioxide: Correlation between the hydrophilic character and surface basicity, *J CO<sub>2</sub> Util* 2018; 26: 171-8.  
<https://doi.org/10.1016/j.jcou.2018.05.006>
- [42] Tang W, Wu Y, Xu A, Gao T, Wei Y, Zhou G. Hybrid porous hypercrosslinking polyanilines: facile Friedel-Crafts preparation, CO<sub>2</sub> capture and Cr(VI) removal properties, *J Porous Mater* 2019; 26: 1495-505.  
<https://doi.org/10.1007/s10934-019-00747-5>
- [43] Yoo DK, Abedin Khan N, Jung SH. Polyaniline-loaded metal-organic framework MIL-101(Cr): Promising adsorbent for CO<sub>2</sub> capture with increased capacity and selectivity by polyaniline introduction, *J CO<sub>2</sub> Util* 2018; 28: 319-25.  
<https://doi.org/10.1016/j.jcou.2018.10.012>
- [44] Aliev SB, Samsonenko DG, Maksimovskiy EA, Fedorovskaya EO, Sapchenko SA, Fedin VP. Polyaniline-intercalated MIL-101: Selective CO<sub>2</sub> sorption and supercapacitor properties, *New J Chem* 2016; 40: 5306-12.  
<https://doi.org/10.1039/C5NJ03477A>
- [45] Tamilarasan P, Ramaprabhu S. Polyaniline-magnetite nanocapsules based nanocomposite for carbon dioxide adsorption, *Int J Greenh. Gas Control* 2012; 10: 486-93.  
<https://doi.org/10.1016/j.ijggc.2012.07.009>
- [46] Kumar Mishra A, Ramaprabhu S. Nanostructured polyaniline decorated graphene sheets for reversible CO<sub>2</sub> Capture, *J Mater Chem* 2012; 22: 3708-12.  
<https://doi.org/10.1039/c2jm15385h>
- [47] Kumar Mishra A, Ramaprabhu S. Polyaniline/multiwalled carbon nanotubes nanocomposite-an excellent reversible CO<sub>2</sub> capture candidate, *RSC Adv* 2012; 2: 1746-50.  
<https://doi.org/10.1039/c1ra00958c>
- [48] Khalili S, Khoshandam B, Jahanshahi M. Synthesis of activated carbon/polyaniline nanocomposites for enhanced CO<sub>2</sub> adsorption, *RSC Adv* 2016; 6: 35692-705.  
<https://doi.org/10.1039/C6RA00884D>
- [49] Peyravi M. Synthesis of nitrogen doped activated carbon/polyaniline material for CO<sub>2</sub> adsorption, *Polym Adv Technol* 2018; 29: 319-28.  
<https://doi.org/10.1002/pat.4117>
- [50] Rodríguez-García S, Santiago R, López-Díaz D, Merchán M, Velázquez MM, Fierro JLG, Palomar J. Role of the Structure of Graphene Oxide Sheets on the CO<sub>2</sub> Adsorption Properties of Nanocomposites Based on Graphene Oxide and Polyaniline or Fe<sub>3</sub>O<sub>4</sub>-Nanoparticles, *ACS Sust Chem Eng* 2019; 7(14): 12464-73.  
<https://doi.org/10.1021/acssuschemeng.9b02035>
- [51] He J, To JWF, Psarras PC, Yan H, Atkinson T, Holmes RT, Nordlund D, Bao Z, Wilcox J. Tunable Polyaniline-Based Porous Carbon with Ultrahigh Surface Area for CO<sub>2</sub> Capture at Elevated Pressure, *Adv Energy Mater* 2016; 6: 1502491(1-11).  
<https://doi.org/10.1002/aenm.201502491>
- [52] Zhang Z, Zhou J, Xing W, Xue Q, Yan Z, Zhuo S, Qiao SZ. Critical role of small micropores in high CO<sub>2</sub> uptake, *Phys Chem Chem Phys* 2013; 15: 2523-9.  
<https://doi.org/10.1039/c2cp44436d>

- [53] Khalili S, Jahanshahi M. Nitrogen doped porous carbon derived from nanofibrous polyaniline for CO<sub>2</sub> adsorption, *J Water Environ Nanotechnol* 2019; 4(4): 285-95.
- [54] Park JM, Woo HC, Jhung SH. Effective CO<sub>2</sub> adsorption at low pressure over nitrogen-enriched porous carbons, derived from melamine-loaded polyaniline, *Chem Eng Sci* 2021; 412: 128641(1-10).  
<https://doi.org/10.1016/j.ces.2021.128641>
- [55] Kemp KC, Chandra V, Saleh M, Kim KS. Reversible CO<sub>2</sub> adsorption by an activated nitrogen doped graphene/polyaniline material, *Nanotechnology* 2013; 24: 235703(1-8).  
<https://doi.org/10.1088/0957-4484/24/23/235703>
- [56] Kutorglo EM, Hassouna F, Beltzung A, Kopecký D, Sedlářová I, Š oš M. Nitrogen-rich hierarchically porous polyaniline-based adsorbents for carbon dioxide (CO<sub>2</sub>) capture, *Chem Eng J*, 2019; 360: 1199-212.  
<https://doi.org/10.1016/j.ces.2018.10.133>
- [57] E. Qezelsefloo, S. Khalili, M. Jahanshahi, M. Peyravi, Adsorptive removal of CO<sub>2</sub> on Nitrogen-doped porous carbon derived from polyaniline: Effect of chemical activation, *Mater. Chem. Phys.*, 239 (2020) 122304(1-12).  
<https://doi.org/10.1016/j.matchemphys.2019.122304>
- [58] Köleli F, Röpke T, Hamann CH. The reduction of CO<sub>2</sub> on polyaniline electrode in a membrane cell, *Synth Met* 2004; 140(1): 65-8.  
[https://doi.org/10.1016/S0379-6779\(03\)00021-3](https://doi.org/10.1016/S0379-6779(03)00021-3)
- [59] Hursán D, Kormányos A, Rajeshwar K, Janáky C. Polyaniline films photoelectrochemically reduce CO<sub>2</sub> to alcohols, *Chem Commun* 2016; 52: 8858-61.  
<https://doi.org/10.1039/C6CC04050K>
- [60] Zhao C, Yin Z, Wang J. Efficient Electrochemical Conversion of CO<sub>2</sub> to HCOOH Using Pd-polyaniline/CNT Nanohybrids Prepared in Situ, *ChemElectroChem* 2015; 2: 1974-82.  
<https://doi.org/10.1002/celec.201500328>
- [61] Li F. Efficient electrochemical reduction of CO<sub>2</sub> to formate using Sn-Polyaniline film on Ni foam, *Electrochim Acta* 2020; 332: 135457(1-8).  
<https://doi.org/10.1016/j.electacta.2019.135457>
- [62] Vijayakumar A, Zhao Y, Zou J, Wang K, Lee CY, MacFarlane DR, Wang C, Wallace GG. A Self-Assembled CO<sub>2</sub> Reduction Electrocatalyst: Posy-Bouquet-Shaped Gold-Polyaniline Core-Shell Nanocomposite, *ChemSusChem* 2020; 13: 5023-30.  
<https://doi.org/10.1002/cssc.202001248>
- [63] Wei X, Yin Z, Lyu K, Li Z, Gong J, Wang G, Xiao L, Lu J, Zhuang L. Highly Selective Reduction of CO<sub>2</sub> to C<sup>2+</sup> Hydrocarbons at Copper/Polyaniline Interfaces, *ACS Catal.* 2020; 10: 4103-11.  
<https://doi.org/10.1021/acscatal.0c00049>
- [64] Rebattet L, Escoubes M, Pinéri M, Geniès EM. Gas sorption in polyaniline powders and gas permeation in polyaniline films, *Synth Met* 1995; 71: 2133-37.
- [65] Aydin R, Köleli F. Electrochemical reduction of CO<sub>2</sub> on a polyaniline electrode under ambient conditions and at high pressure in methanol, *J Electroanal Chem* 2002; 535: 107-12.  
[https://doi.org/10.1016/S0022-0728\(02\)01151-8](https://doi.org/10.1016/S0022-0728(02)01151-8)
- [66] Chou CT, Huang CH, Cheng NC, Shen YT, Yang HS, Yang MW. Adsorption processes for CO<sub>2</sub> capture from flue gas using polyaniline solid sorbent, *RSC Adv.* 2014; 4: 36307-15.  
<https://doi.org/10.1039/C4RA04333B>
- [67] Radosz M, Hu X, Krutkramelis K, Shen Y. Flue-Gas Carbon Capture on Carbonaceous Sorbents: Toward a Low-Cost Multifunctional Carbon Filter for "Green" Energy Producers, *Ind Eng Chem Res* 2008; 47: 3783-94.  
<https://doi.org/10.1021/ie0707974>
- [68] Himeno S, Komatsu T, Fujita S. High-Pressure Adsorption Equilibria of Methane and Carbon Dioxide on Several Activated Carbons, *J Chem Eng Data* 2005; 50(2): 369-76.  
<https://doi.org/10.1021/je049786x>
- [69] Cinke M, Li J, Bauschlicher Jr CW, Ricca A, Meyyappan M. CO<sub>2</sub> adsorption in single-walled carbon nanotubes, *Chem Phys Lett* 2003; 376: 761-6.  
[https://doi.org/10.1016/S0009-2614\(03\)01124-2](https://doi.org/10.1016/S0009-2614(03)01124-2)
- [70] Su F, Lu C, Chen W, Bai H, Hwang JF. Capture of CO<sub>2</sub> from flue gas via multiwalled carbon nanotubes, *Sci Total Environ* 2009; 407: 3017-23.  
<https://doi.org/10.1016/j.scitotenv.2009.01.007>
- [71] Zhang Z, Zhou J, Xing W, Xue Q, Yan Z, Zhuo S, Qiao SZ. Critical role of small micropores in high CO<sub>2</sub> uptake, *Phys Chem Chem Phys* 2013; 15: 2523-9.  
<https://doi.org/10.1039/c2cp44436d>

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