Doped-polyaniline based sorbents for the simultaneous removal of heavy metals and dyes from water: unravelling the role of synthesis method and doping agent

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Abstract

Recently, the engineering of alternative adsorbents with better functional and sorbing ability towards the purification of wastewaters has received much attention from the scientific community. Currently polymers, in particular, are regarded as attractive soft materials in the field of environmental remediation due to their several unique properties. In this regard, the synthesis method is key point to fabricate polymer-based adsorbent with targeted characteristics. In the present work, four polyaniline (PANIs) samples were synthesized by two alternative chemical approaches, a traditional one and an eco-friendly one, and two different dopants were used, HCl and H_2SO_4, respectively. All PANIs were characterized for their thermal, optical, morphological, and structural properties and their capability to remove simultaneously dyes and heavy metals from water have been investigated. It was deduced that the sorption ability is dependent on the as-synthesised PANI using different procedures and dopants. All the PANIs from traditional method showed high levels of pollutants removal (from 89 to 97%). Even though the materials obtained from the green way are overall less active, H_2SO_4-doped corresponding polymer showed high sorption capability (75-97%). Finally, the most performing PANIs were selected for recycling tests exhibiting high sorption efficiency retention up to four runs without any regeneration treatment.

Most important, the cycling tests were stopped well before the sample sorption limit could be reached.

Keywords: pollutants abatement, polyaniline, sorption, dopants, dyes, heavy metals.

1. Introduction

Because of the intensification of industrial activities and the rapid global population growth from 300 to 500 million tons of solvents, heavy metals, toxic sewage sludges and other industrial waste are released every year in water [1]. Among the numerous aqueous pollutants, dyes and heavy metals occupy a special place due to their high toxicity and diffusion. The presence of dyes in water bodies causes an increase of the biochemical oxygen demand (BOD) level and reduces the light penetration with dramatic consequences on the aquatic life as well as on human and animals' health. Dyes find application in different fields, for coloring fibers (cotton, wool, silk, nylon, synthetic fibers), paper, plastics, paints, inks, etc., but also in the sector of food, cosmetics, gasoline, lubricants, oils, soaps, and detergents and so on [2]. Similarly, heavy metals represent another class of toxic pollutants finding application in various industrial sectors, such as metal plating, mining, leather, fertilizer industries, and, as a consequence, every year directly or indirectly a large number of these pollutants, mainly zinc, copper, nickel, arsenic, lead, cadmium, chromium, mercury, and cobalt, enter the environment through the industrial wastewater discharge. It is known that toxic metals can enter the human body and their accumulation has been linked to the onset of various diseases and illnesses [3]. Therefore, the production of large volumes of dye and heavy metals-loaded wastewaters, in particular in countries where environmental regulations are not very restrictive, represents great worry from the human and ecological point of views as well.

Over the last decades, a number of methods for the removal of pollutants from water and wastewater has been developed, such as coagulation, filtration with coagulation, ion exchange, etc. [2]. Among them, sorption on a solid support represents a very effective and competitive approach for waste abatement, since it can be performed under mild conditions without the addition of expensive catalysts, oxidants, light irradiation and so on [4]. To date, various types of sorbents have been developed ranging from porous carbons [5] to mesoporous materials [6], passing from metal-organic frameworks (MOFs) [7], carbon nanotubes (CNTs), graphene, biochar and activated carbon (AC) [8]. This latter is the most used support thanks to its high surface area, high porosity and low selectivity [9]. The main disadvantage of this material is the necessity to activate and regenerate it through thermic treatment at high temperature or using solvents, causing additional costs. Recently, innovative materials have been investigated for this kind of application, such as polymeric membranes [10, 11] and metal oxides [12], although they suffer from some limitations.

Conducting polymers (CPs), such as polyaniline (PANI), polypyrrole and polythiophene, represent interesting alternatives to traditional sorbents and have received significant attention in particular for the removal of different pollutants [13-16].

Among the CPs, PANI is unique for its peculiar characteristics, as ease of synthesis, high stability and interesting redox properties [17, 18]. A large number of papers has been published on the ability of PANI and its composites to remove dyes and heavy metals [19-30].

However, in all these cases PANI is always synthesized by different approaches and a comparison among the various performances is useless.

Furthermore, all these works deal with different pollutants individually and none of these face the issue of selectivity in the sorption process or investigate possible interferences due to the presence of different species. It is worth noting that for application in large-scale easy, cheap, and fast synthetic approaches are to be preferred to more sophisticated methods. Moreover, since the chemical-physical properties of PANI are strongly related to numerous factors, ranging from the type of synthetic procedure to the kind of dopant, there are as many PANIs as the routes leading to their manufacture. The scientific literature is lacking from this point of view, while an in-depth study is necessary for clarifying the effect of synthetic strategy and dopant on the material sorption capability. This will contribute to tailor methods according to the required application.

The present work aims to investigate the effect of both the dopant and the synthetic route on the capability of PANI to remove either dyes or metals from water. Two inorganic doping agents were chosen (HCl and H_2SO_4), for their wide use in PANI synthesis, and two easy and fast synthetic approaches were compared consisting in chemical polymerization. Moreover, the most performing materials were selected for the removal of pollutants mixtures. We demonstrated that each variation in the polymer preparation entails differences on its sorption behavior, whereas even in the presence of pollutants mixture the polymer maintains high sorption efficiency.

2. Materials and methods

For all the experimental procedures Merck reagents were adopted. For the preparation of all the solutions ultrapure (UP) water was used.

PANI was prepared by two different approaches, a traditional procedure [31] and an environmentally friendly strategy [15], using both HCl and H_2SO_4 and as the doping agents.

2.1. Synthesis of PANIs1

1 g of aniline was introduced in a 500 mL flask containing 250 mL of UP water. The flask was placed in an ice bath. Then, 9 mL of HCl 37% (w/w) (molar ratio HCl/aniline 10:1) were added under stirring. After this, the solution was stirred for other 30 minutes in the ice bath.

Meantime, it was prepared a solution containing a proper oxidant dissolving 4.3 g of $K_2S_2O_8$ into 100 mL of UP water (molar ratio $K_2S_2O_8$/aniline 1.5:1). This solution was added drop by drop into the solution containing aniline. When the addition was finished, the ice bath was removed, and the mixture was stirred at room temperature for 6 h.

Then, the reaction was stopped through the addition of a few milliliters of acetone and the obtained solid (PANI1/HCl) was recovered by filtration, abundantly washed with UP water and acetone until the mother liquor becomes colorless, and finally dried at air, weighed, and grounded in a mortar.

PANI1/H_2SO_4 was synthesized using the same procedure, replacing the HCl solution with 5.0 mL of H_2SO_4 at 95% (w/w) as the dopant.

The polymerization yield for both PANI1/HCl and PANI1/H_2SO_4 was 70% and 95% respectively.

2.2.Synthesis of PANIs2

1 g of *N*-4-(aminophentl)aniline (aniline dimer) was grounded in a mortar and, then, dissolved in 250 mL of UP water acidified with 2.27 mL of HCl 37% (molar ratio HCl/aniline dimer 5:1).

The obtained mixture was stirred for 1 h until complete dissolution of aniline dimer.

Then, 2.35 mL of H_2O_2 30% w/w (molar ratio H_2O_2/aniline dimer 5:1) and 0.15 mL of solution of $FeCl_3$ ([Fe^{3+}] = 5 mg/mL) were added in rapid succession.

The reaction mixture was stirred for 24 h and then it was stopped by the addition of a few milliliters of acetone, as described above for PANI1. The obtained powder (PANI2/HCl) was recovered by filtration, abundantly washed with UP water and acetone until the mother liquor becomes colorless, and finally dried at air, weighed, and grounded in a mortar.

PANI2/H_2SO_4 was synthesized using the same procedure, replacing HCl with 1.4 mL of H_2SO_4 at 95% (w/w).

The polymerization yield for both PANI/HCl and PANI/H_2SO_4 was 85% and 93%, respectively.

2.3. Characterization

Each synthesized material was characterized trough ultraviolet-visible spectroscopy (UV-vis), Fourier transformed infrared spectroscopy (FT-IR), X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA). Moreover, the specific surface area and the point of zero charge (PZC) was determined.

UV-vis spectroscopy analyses were performed using a spectrophotometer Hewlett Packard HP8453. A small amount of each sample was dissolved in a few mL of *N*,*N*-dimethylformamide and, then, analyzed. The spectra were acquired in the range 190 - 1000 nm, with a resolution of 1 nm and with an optical path length of 1 cm.

FT-IR spectroscopy analyses were performed using a Jasco FT-IR 410 spectrophotometer. A few milligrams of each material were homogeneously dispersed in anhydrous KBr and pressed it to obtain a thin pellet. The spectra were recorded in the range 400 - 4000 cm-1 with a resolution of 0.5 cm^{-1}.

XRPD investigations were performed using a Rigaku D III-MAX diffractometer equipped with a Cu lamp. The diffractograms were acquired in the range of 10-50 2theta.

SEM analyses were carried out using a LEO 1430 scanning electrone microscope.

TEM analyses were conducted by a TEM LEO 912AB microscope.

TGA analyses were performed using a Perkin Elmer TAC 7/DX analyzer under nitrogen flow. A few milligrams of each sample were weighted in a platinum pan and heated in the range 50°C - 900°C with a heating rate of 10°C/min.

The specific surface area of each material was determined by the Brunauer-Emmett-Teller (BET) method from adsorption isotherms of N_2 in subcritical conditions using a SA3100 instrument (Beckman-Coulter, Brea, CA, USA).

The point of zero charge of each material was carried out by the solid addition method [32]. 50 mg of each sample was suspended in 50 mL of 0.001 M NaCl solutions at various pH (2-10) under stirring. The initial pH (pH_i) of the solution was adjusted using 0.1 M HCl or NaOH. After 24 h, the pH value of the supernatant was measured. The difference between the final and initial pH ($\Delta pH = pH_f - pH_i$) was plotted against the pH_i. In the plot, the point of intersection of the resulting curve at which $\Delta pH = 0$ was the pH_{PZC} value.

2.4. Sorption tests

All the synthesized materials were tested as sorbents for the removal of organic dyes (methylene blue MB, acid green AG) and heavy metals (lead, cadmium, chromium) from UP water.

For the sorption tests 50 mg of each PANI were introduced in 20 mL of aqueous solution containing one of the previously specified pollutants or a mixture of them (lead + cadmium, lead + MB). The concentration of each pollutant in solution was 10 mg/L. The mixture was stirred for 30 minutes at room temperature. A series of experiments was carried out without pH control, whereas for other tests the pH value of the solution was properly corrected by the addition of a few drops of HCl or NaOH 0.1M and 0.01M until to reach a constant value of 2 or 10 depending on the treated pollutant. Then, PANI was separated from solution by centrifugation, and reused to perform recycle studies.

For the analysis of the dyes in the final solutions UV-vis spectroscopy was used. For MB detection λ = 667 nm. For AG analysis from solution at pH 2, λ was 619 nm, whereas for the analysis of solutions at spontaneous pH (that is the pH of the solution after the addition of PANIs, which resulted to be about 3.3 pH for all the samples) λ was 601 nm. UV-vis spectroscopy and atomic absorption spectroscopy (AAS) were employed for the quantification of heavy metals in solution. The lead and cadmium concentration in each solution was evaluated by AAS (λ = 283.3 nm for lead, λ = 228.8 nm for cadmium). The total amount of chromium (Cr(III) and Cr(VI)) was analyzed by AAS (λ = 357.9 nm), whereas Cr(VI) was evaluated by UV-vis spectroscopy by diphenylcarbazide method [21].

Each experiment was repeated three times.

2.5.Recycling tests

Recycling studies were carried out on those PANIs that gave the best performances. In detail, after the first sorption test, PANI was separated from the solution by centrifugation and reused in the same conditions without any post-treatment. Four recycle tests were performed for each material.

Each experiment was repeated three times.

3. Results and discussion

Four PANIs were synthesized by two easy synthetic approaches, both based on chemical oxidative polymerization reactions: a traditional way [33] (PANI1) and an environmentally friendly route (PANI2) [15]. Two different widely used mineral acids were added as the doping agents: HCl and H_2SO_4. The final materials were properly characterized and tested for the abatement of both cationic and anionic dyes and heavy metals and their mixtures.

3.1. Materials Characterization

Since, as reported in the literature [34], the chemical-physical properties of PANI are critically depending on the reaction conditions employed, such as temperature, concentration of reagents, pH of the solution, kind of doping agent, etc., all the synthesized PANIs were thoroughly characterized before their use as sorbents. The infrared spectra of all synthesized materials are very similar, as shown in Figure 1 A. In fact, all materials display the characteristic bands of PANI in form of conducting emeraldine salt, as detailed in Table 1.

Table 1. Characteristic bands for PANI in the FT-IR spectra of Figure 1 A.

Wavenumber (cm^{-1})	Assignment
3400-1800 (broad band)	Highly conjugated structures [35]
1570	C=C stretching vibration of quinoid rings [16]
1490	C=C stretching vibration of benzenoid rings [16]
1304	C-N stretching vibration modes [16]
1240	$C\text{-}N^{+\bullet}$ stretching vibration modes [35]
1146	$Q{=}NH^{+}\text{-}B$, $B\text{-}NH^{+}\text{-}B$ [36]

820-800	C-H out-of-plane bending vibrations of 1,4-disubstituted aromatic rings [37]
800 and 759	C-H vibrations of 1,2,4-trisubstituted and 1,2-disubstituted rings [37]

Q = quinoid ring, B = benzenoid ring

The UV-vis spectra of the polymers, displayed in Figure 1 B, present two main absorption bands: a first one with a maximum at about 320 nm, corresponding to π-$\pi*$ transition, and another one at about 630 nm, related to molecular excitation transition [16]. The red shift of the second band in the UV-vis spectra of PANIs1 can be associated to a different oxidation degree of the polymeric chains, higher for PANIs1 than for PANIs2 [38].

If on the one hand all the materials exhibit very similar chemical structures, as confirmed by the FT-IR and UV-vis spectra (Fig. 1A and 1B), on the other hand interesting differences in terms of crystallinity degree (Fig. 1C) and thermal stability (Fig. 1D) were observed.

Concerning the crystallinity, all the PANIs show ES-I (emeraldine salt-I) pseudo-orthorhombic crystalline structure, according to the literature [39]. Three peaks centered at 2θ ~15° (011), ~20° (100) and ~ 25° (110) can be observed in the XRPD patterns of HCl-doped PANIs and PANI1/H_2SO_4. However, some interesting differences can be observed. The XRPD patterns of the two PANIs1 are completely overlapping, whereas that of PANI2/HCl shows more defined and intense peaks.

Finally, a different crystallinity emerges from the XRPD pattern of PANI2/H_2SO_4. Even though some authors attribute the decrease in crystallinity to the molecular size of the doping agent used [40], it is evident that this cannot be the unique reason. Other factors seem to be involved, such as the synthetic approach used for the polymers production. In fact, very similar degree of crystallinity was observed for the two PANIs synthesized by the traditional method. In this case, the kind of doping agent employed seems to have no effect on the crystallinity degree of the final material. Although in this regard differences were reported by other authors, it is important to underline that they refer to materials prepared under diverse conditions: biphasic system [41], high temperature [42] or without stirring [43].

On the contrary, for PANIs from the "green" way the type of dopant introduced in the reaction mixture plays a key role on the crystallinity of the polymer. PANI2/HCl shows a very similar crystallinity compared to PANIs1, only slightly higher, characteristic of ES-I structure [39]. However, when H_2SO_4 is used as the doping agent, the polymer exhibits the characteristic XRPD pattern of EB-II crystalline structure [39]. In this regard, it is important to take into consideration that the polymerization reaction carried out by the environmentally friendly approach is faster than the traditional one [15] and the possibility to control the growth of the polymeric chains is scarce. As a consequence, a fast and irreversible rearrangement of PANI chains as a function of the dimension of the counterion could occur, whereas in the case of the traditional synthesis this process is slow and can be strongly controlled. Figure 1D shows the thermogravimetric curves obtained under an N_2 atmosphere for all the PANI samples. The results display three major steps of weight loss for each PANI sample related to water loss (at about 100 °C), dopant loss (at about 200°C for HCl and at about 300°C for H_2SO_4) and backbone decomposition (300-500°C depending on the type of PANI).

The thermogravimetric analyses demonstrated that the first weight loss is higher for PANIs1 than for PANIs2, indicating that the moisture content inside these latter is lower. Above about 500°C the polymer carbonization of all the materials takes place. As shown in Figure 1D, the thermal stability of the PANIs follows this trend: PANI1/HCl ≈ PANI2/H_2SO_4 > PANI2/HCl > PANI1/H_2SO_4. Only for this latter material a complete decomposition was observed. Many factors can contribute to the different behavior of the four polymers, ranging from molecular weights of the polymeric chains to changes in the molecular structure or cross-linking phenomena [44]. This kind of investigation is beyond the scope of this work, but a deepening in this sense would be important. However, the results obtained for PANIs1 are in agreement with the data presented in the literature [45] which report a lower thermal stability of the polymer when doped with H_2SO_4 as well as a more compact morphology (Fig. 2). The different trend observed for PANIs2 confirm that the different synthetic conditions (different reagents and oxidants) strongly affect the properties of the final polymers.

Figure 2 reports both the SEM and the TEM images of the PANIs.

As for XRPD and TGA, also for the morphology both the synthetic approaches and the dopants employed seem to have an effect on the characteristics of the materials. More in details, PANIs1 show quite porous surface morphologies characterized by coral-like structures generating microchannels throughout the material (Fig. 2 A, C, E and F). According to the literature [45], passing from HCl to H_2SO_4 aggregation phenomena occur, as confirmed by the values of surface area (Table 2).

Table 2: BET surface area of the four PANIs.

Sample	**BET surface area (m^2/g)**
PANI1/HCl	32.05
PANI1/H_2SO_4	10.20
PANI2/HCl	2.05
PANI2/H_2SO_4	2.95

It was demonstrated that the coral-like structures observed for HCl-doped PANI1 can be related to a homogenous polymerization characterized by a spontaneous self-nucleation during oxidative polymerization [46-48]. On the contrary, when H_2SO_4 is used as the dopant, a heterogeneous polymerization takes place and at the beginning different polymerized aniline chains grow in solution separately. Then, these hetero nuclei particles link each other leading to the agglomerated morphology.

On the other hand, as discussed above, PANIs2 showed a highly compact morphology both using HCl and H_2SO_4 as the dopant, caused by the fast growth of the polymeric chains during the polymerization reaction that makes hard any structural or morphological control of the polymer.

The sorption of chemical species onto the surface of sorbents depends on two main factors: electrical charge of the two chemical species (surface charge of the sorbent, charge of the pollutant) and on the pH of the system.

The point of zero charge (PZC) describes the condition when the electrical charge density on a surface is zero. For the synthesized materials PZC is reported in Figure 3 and the PZC values for each polymer was derived from the intercept of the linear relations between ΔpH (pH_f – pH_i) and pH_i.

The four polymers showed PZC at a pH of 3.50 (PANI1/Cl), 3.01 (PANI1/H_2SO_4), 4.11 (PANI2/HCl) and 4.25 (PANI2/H_2SO_4) respectively. For all the PANIs, at pH below pI (pH at PZC) nitrogen atoms, mainly the imine groups, easier to be protonated than the amine groups [49], can be protonated making the PANIs carrying positive charge. It is interesting to note that for PANIs2 pI is slightly higher than for PANIs1. These results confirm those obtained by the UV-vis spectra (Figure 2B), that demonstrated a slightly higher oxidation level for PANIs1, which results in a greater number of imine groups in the polymer chains. At pH values below the point of zero charge (pH_{PZC}), the polymers surface is positively charged, whereas at pH values higher than the pH_{PZC} they are negatively charged. Based on these results, it is possible to predict variation of the sorbents performances as a function of the pH of the solutions and the charge of the pollutants. In fact, positively charged surfaces promote the sorption of the anionic pollutants, whereas when the sorbents are negatively charged the removal of cationic species is promoted.

The results obtained for the four PANIs were consistent with the change of sorption capacities at different pH, as described below.

3.2. Sorption tests

All the PANIs were used as sorbents for the removal of two classes of pollutants from water: dyes and heavy metals. The dye sorption capability was tested towards both AG, as a model of anionic dye, and MB as a model of cationic dye, at spontaneous pH (pH of the solution after the addition of PANI, about 3.3) and after pH optimization, as shown in Figure 4 A and B.

Concerning AG removal, all the materials exhibit good activity when used at spontaneous pH. In fact, as confirmed by the PZC values, under these conditions (spontaneous pH about 3.3 for all the polymers) PANIs are completely protonated, and the anionic dye is easily adsorbed *via* electrostatic attraction. As expected, the more oxidized PANIs1, characterized by higher values of surface area, display greater performances. Surprisingly also the more compact PANIs2 exhibit a certain activity.

In fact, surface area is not the unique factor at play. Although the main PANI sorption mechanism consists in an anion-exchange process (dopant anion *vs*. anionic dye), the second one, based on short-range interactions such as hydrogen bonding and π-π stacking [50, 51], at spontaneous pH become important between the $=NH_2^+$- groups of PANI and the anionic dye. On the contrary, under these conditions, cationic dyes, such as MB, cannot be easily removed (Figure 4B) even though PANI1/Cl maintains a certain degree of activity that can be attributed to its high surface area, permitting both π-π and electrostatic interactions between the $=N^+(CH_3)_2$ terminal groups of the dye and the amine sites of the polymer. For all the other materials, electrostatic repulsion between both the positively charged sites of PANI and dyes prevails. It is known that the pH of the medium also plays a critical role in the sorption processes [52]. Therefore, we tried to improve the sorption ability of the polymers towards the two dyes modifying the initial pH of the solution by addition of proper quantity of HCl or NaOH. Two pH values were investigated: 2 for the anionic dye (AG) and 10 for the cationic one (MB). Concerning the AG abatement, for almost all the PANIs the pH decrease caused a reduction in their removal capabilities of about 24% (only PANI2/H_2SO_4 showed a reduction of 13%). Since pH optimization was carried out by means of small addition of HCl, the excess of chloride ions in solution could compete with anion dyes for the positively charged sites of PANI. Moreover, the higher ionic strength could influence the equilibrium anion-charged sites.

Strong alkaline conditions are essential to convert the positive charged sites of the polymers into basic sites (amine and imine groups) to make PANI active in the cationic dye sorption, as confirmed by the tests carried out at pH 10 for the removal of MB. The complete inactivity of PANI2/HCl can be easily ascribed to its very low surface area.

By the same approach, the sorption capabilities of PANIs were also tested for the removal of toxic and carcinogenic cationic (Pb^{2+} and Cd^{2+}) and anionic ($HCrO_4^-$) metals, to compare the PANIs sorption abilities towards both organic and inorganic pollutants. As shown in Figure 4C, alkaline conditions are required for the removal of cationic metals as already observed for cationic dye. Both in acidic (spontaneous pH) and in alkaline conditions a slightly higher sorption towards Cd^{2+}

compared to Pb^{2+} was observed, probably related to the different ionic radii of the two ions (1.19 Å for Pb^{2+} and 0.97 Å for Cd^{2+}). Moreover, in this case, also the highly compact PANI2/HCl was active, probably thanks to the very low dimension of these species that can easily access the active PANIs sites.

It is worth noting that the distribution of both the Cd(II) and Pb(II) species is affected by pH changes. If on the one hand, at low pH values the main species in solution are Pb^{2+} and Cd^{2+}, on the other hand, at very high pH values (> 10) negative charged species prevail ($Pb(OH)_3^-$ and $Cd(OH)_3^-$ respectively), which cannot find active sites on the surface of emeraldine bases.

At pH 10 it is possible to ensure the presence of not-charged species in solution ($Pb(OH)_2$ and $Cd(OH)_2$ respectively). However, under these conditions, the solubility of the two hydroxides has to be taken strongly into account.

In fact, at this pH level the solubility of $Pb(OH)_2$ is very poor, whereas $Cd(OH)_2$ remains in solution as a solid suspension. Therefore, the high percentage of metals removal observed in alkaline condition can be easily attributed to a surface precipitation of the metals as the insoluble hydroxides on the surface of the sorbents.

Concerning Cr(VI) abatement from water matrix, chemical reduction of this pollutant to the less toxic Cr(III) form is the most widely used approach, followed by the removal of the latter by sorption or precipitation as $Cr(OH)_3$ and filtration. As reported in the literature [53], PANI can remove hexavalent chromium by both sorption (anion exchange on the surface of the polymers between the dopant anion and $HCrO_4^-$) and reduction processes. In Figure 4D we compare the performances of all the polymers in terms of sorption and reduction abilities both at spontaneous pH and at pH 2. For all the materials under all the investigated conditions both the mechanisms are involved. In general, all the polymers show high abilities in the Cr(VI) abatement in both the pH values investigated. In particular, thanks to its high surface, PANI1/HCl displayed always higher sorption capabilities than the other materials which, on the contrary, showed a more pronounced production of Cr(III). This latter mechanism is the only one involved when PANI1/H_2SO_4 is used as the sorbent at pH 2.

It is interesting to note that the ability of PANI towards Cr(VI) abatement can be easily tuned playing not only on the synthetic conditions of the polymer but also on the pH of the matrix.

Assessing the nature of the species adsorbed on the materials (Cr(III) and Cr(VI)) and their amount would help to better understand the processes underlying the removal mechanism. However, these aspects overlook the purpose of this work.

Although the scientific literature reports numerous studies dealing with aqueous pollutants removal by PANI (Table 3), a real comparison of the materials performances is not possible [22-29].

Table 3 summarizes some of the best results reported recently and those of the present work, obtained using easily synthesized PANIs powders.

Table3: PANIs dyes and heavy metals removal capability.

Kind of PANI	**Pollutant**	**Adsorption capacity (%)**	**References**
Phytic acid-doped PANI nanofibers	Cu(II)	72	22
PVDF-HFP/PANI membranes	Cr(VI)	70	23
PANI nanofibers	Methylene blue	91	24
PANI/H_2SO_4	Direct blue 78	80.2	25
PANI/H_3PO_4	Direct blue 78	89.3	25

PANI/HNO_3	Direct blue 78	76.5	25
PANI hollow sphere	Methyl orange	60	26
Polyacids doped-PANI	methylene blue (MB) and rose bengal (RB)	(MB) 95, (RB) 95	27
H_2SO_4-doped PANI	Cr(VI)	99.43	28
HCl-PANI	Cr(VI)	100	29
Surfulamic acid-doped PANI	Cr(VI)	100	29
PANI/HCl powder (traditional method)	MB, Acid green (AG), Cd(II), Pb(II), Cr(VI)	(MB) 97, (AG) 96, (Cd II) 96, (Pb II) 89, (CrVI) 94	This study
PANI/HCl powder (green method)	MB, Acid green (AG), Cd(II), Pb(II), Cr(VI)	(MB) 82, (AG) 1, (Cd II) 96, (Pb II) 81, (CrVI) 100	This study
PANI/H_2SO_4 powder (traditional method)	MB, Acid green (AG), Cd(II), Pb(II), Cr(VI)	(MB) 98, (AG) 98, (Cd II) 96, (Pb II) 89, (CrVI) 96	This study
PANI/H_2SO_4 powder (green method)	MB, Acid green (AG), Cd(II), Pb(II), Cr(VI)	(MB) 75, (AG) 91, (Cd II) 97, (Pb II) 93, (CrVI) 86	This study

Noteworthy, in these works the polymer was always synthesized by different approaches leading to materials characterized by diverse morphology and chemical-physical characteristics. Furthermore, the removal of a different single pollutant was always investigated. Herein, for the first time, the performances of different PANIs have been evaluated towards the removal of different pollutants, demonstrating that many parameters affect the sorption process depending on the type of material. All materials exhibited excellent removal abilities, although PANIs1 were superior to PANIs2.

3.3. Recycling tests

The possibility to regenerate and reuse sorbent materials is crucial for reducing waste production and process costs. The polymers that showed the best performances on pollutants removal were selected for four recycling tests and the results are summarized in Figure 5.

As it is possible to observe, a good reproducibility of the materials performances was observed after**.** Only in the case of hexavalent chromium abatement an important difference in the polymer behaviour was noted over the tests. In fact, during the 5 consecutive runs, the polymer gradually lost its reducing capacity strictly related to the number of imino-quinoid segments present in its structure. Conversely its absorbent capacity remained unaltered, thus indicating that the material had not yet reached saturation.

3.4. Sorption of mixtures of pollutants

PANI2/H_2SO_4, synthesized by environmentally friendly approach, resulted to be particularly promising inboth dyes and metals abatement. Hence, it was selected in the removal of simple mixtures of pollutants to assess its selectivity (here defined as the discrimination shown by the sorbent towards different pollutants that compete for the active sites of the material). Since, as previously demonstrated, the ability of PANI to remove cation or anionc pollutants is strongly dependent on the solution pH, we decided to investigate PANI capability to remove mixures of cationic pollutants at pH 10 (Fig. 6).

Figure 6 shows that when the material is put in contact with a mixture of Pb^{2+} and MB, it does not exhibit any selectivity, whereas in presence of the two metals (Pb^{2+} and Cd^{2+}) higher selectivity towards Pb^{2+} is surprisingly observed. It is important to remember that, under the alkaline conditions of the sorption test, both the metals are in form of poor soluble or insoluble hydroxides that precipate on the polymer surface therefore modifying its characteristics.

Conclusions

The scientific literature reports several examples of PANI-based sorbents for both dyes and metals abatement. However, a critical evaluation of the performances based on the polymer chemical-physical properties is not possible. In fact, although PANI represents a very promising material for this kind of application due to notable results recently reported, the use of materials in such different morphologies (nanospheres, nanofibers, nanotubes, micro-sized powders, etc.) make hard any conclusion. These textural and morphological properties are indeed strongly related to several factors, such as method of synthesis, type of doping agent, temperature and concentration of reagents. Moreover, in view of large-scale application, easy, cheap, and fast synthetic approaches are preferable to more sophisticated methods. If on the one hand these latter generally guarantee a high control of the material properties, on the other hand lack in terms of practical application because of low polymerization yield and difficult recovery of the material. In order to investigate the effect of both synthetic method and dopant on PANI characteristics and on its ability to act as sorbent for the removal of dyes and heavy metals from water matrix, an in-depth assessment was carried out. A comparison between two oxidative chemical polymerization reactions, a traditional one and a "green" one, was performed. These two synthetic routes differs mainly for the type of reagents (aniline and aniline dimer as starting materials) and dopants (HCl and H_2SO_4) employed. It was demonstrated that, athough the synthesized polymers showed a very similar chemical structure, PANIs from the traditional method are characterized by a higher oxidation level, that contributed to PZC at lower pH values. In terms of morphology PANIs obtained by the traditional method are characterized by coral-like structures that tend to aggregate when the reaction is carried out in the presence of H_2SO_4. On the contrary, a fine control of the morphology for PANIs from "green" approach is not possible because of the fast polymerization reaction, leading to compact materials characterized by low values of surface area. All the polymers resulted to be promising candidates for both dyes and heavy metals removal from aqueous solutions and retained their high activity even after a 4-run recycling. Acidic conditions are required for the removal of both organic and inorganic anions, whereas alkaline solutions promote the abatement of cationic pollutants. Moreover, the kind of dopand employed for the synthesis of the material plays an important role not only to tune its chemical-physical characteristics but also to modify its reducing capability towards Cr(VI). In fact, PANI1/H_2SO_4 showed the highest activity in Cr(VI) reduction, that gradually decreases after a 4-run recycling, whereas all the polymers maintain good sorption capability. For the first time, the sorption ability of PANI was tested for the removal of mixtures of pollutants, demonstrating low selectivity toward the species investigated. Despite the interesting results obtained, much remains to be understood on the mechanisms that polyanilines employ for water depollution and especially on their behavior in the presence of mixtures of pollutants or complex matrices.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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