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Chemical synthesis and characterization of polyaniline: Water depollution efficiency and effectiveness

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ABSTRACT

This study focuses on the chemical synthesis of polyaniline (PANi) in the presence of sodium persulfate in a hydrochloric acid medium. The characterization of synthesized PANI was carried out using scanning electron microscopy (SEM), infrared spectroscopy (IR), X-ray diffraction (XRD), X-ray photoelectrons spectroscopy (XPS) and thermal analysis. Adsorption experiments of organic and inorganic water pollutants (pharmaceutical products, dyes, derivatives of humic acids and heavy metals) were carried out in a batch reactor. The obtained results indicate that the synthesized PANi led to an almost complete removal (~100%) of these compounds from aqueous solution.

Keywords: Adsorption; Chemical synthesis; Polyaniline; Polymerization; Water treatment.

1. Introduction

The polyaniline (PANi) is considered as one of the most widely used materials. This is due to its excellent stability, good redox reversibility and increased electrical conductivity [1,2] that renders it effective for several applications such as the metallization of insulators, the coating of sensors for vapours and toxic gases analysis, the coating of oxidizable metals and protection against corrosion, the development of fuel cells and the treatment of industrial effluents [3–7].

The PANi exists under different oxidation states [8–12]. One of these is the leucoemeraldine-base which is a white solid completely reduced and readily oxidisable. It is composed of 100% of benzene diamine. The second form is the emeraldine basis (semi-oxidized form), which is a solid blue and the pernigraniline base which is a solid red that is totally oxidized and composed 100% of quinonediimine. The latter may easily undergo hydrolysis in acidic medium. The most stable structure of PANi, in ambient conditions, is composed of 50% of the reduced form of benzene diamine and 50% of the oxidative form of quinine diimine.

In the past decades, the water pollution has increased significantly and become the most environmental issue, which can cause serious damage to the human health and biodiversity. The industrial effluents are the major source of aquatic pollution. The toxicity and non-biodegradability are the most common characteristics of the majority of industrial pollutants such as dyes, heavy metals, drug residues and humic acids derivatives [13–15]. The removal of these toxic compounds from wastewater is a major challenge for future generations. To solve this environmental problem, many scientists worldwide have paid great attention in order to remove the pollutant substances from water. In this context, several techniques such as chemical precipitation, coagulation, membrane filtration, photocatalytic degradation and adsorption have been used for wastewater treatment [16–20]. Among these technologies, the adsorption is widely used because of its distinct advantages such as the simplicity to operate, low cost, flexibility and high effectiveness [21].

In this work, the optimum chemical synthesis of PANi is pursued towards its application for wastewater treatment by a multitude of organic and inorganic pollutants.

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All synthesized PANi were characterized by different analytical techniques and tested for their adsorption capacity against drug residues (sodium salicylate), industrial dyes (Congo red and Carmine indigo), humic acids derivatives (hemimellitic, trimellitic and pyromellitic acids) and heavy metals (Cr(VI)).

2. Materials and methods

2.1. Synthesis of PANi

The oxidation of aniline by sodium persulfate in an acidic environment was performed according to the reaction illustrated in Fig. 1. The synthesis of PANi in the laboratory was carried according to the method proposed by MacDiarmid [22]. Specifically, a well-mixed solution of sodium persulphate (0.015 mol) was added drop by drop to an aqueous solution of hydrochloric acid (1 M) containing the aniline (0.02 mol) with a molar ratio (monomer/oxidant) (1.5/1). The mixture was finally shaken for 2 h. The reaction medium was initially blue-green and then evolved toward a green dark powder. The powder was washed with distilled water and ethanol. Finally, the obtained polymer was dried in an oven at a temperature of 60°C.

2.2. Characterization

The structure of the PANi has been investigated in different experimental conditions of synthesis such as temperature, time of polymerization and mode of oxidant addition. The PANi was characterized by scanning electron microscopy (ESEM FEI Quanta 200) in order to obtain the visual information about the adsorbent morphology. The Fourier transforms infrared spectroscopy (FTIR Vertex 70) was used to identify the molecular structure of the PANi. Furthermore, the X-rays diffraction (XRD, EMPYREAN PANALYTICAL diffractometer) was used to determine the arrangement and the orientation of chains within the polymer. The synthesized PANi was also analyzed by X-ray photoelectron spectroscopy (XPS, Shimadzu Co: AXIS ULTRA).). The thermal analysis of PANi was carried out using thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) (Shimadzu D60) in a temperature range of 25–600°C with the heating rate 10°C/min at air atmosphere.

2.3. Adsorption experiments

The adsorption of several pollutants such as Congo red, Carmine Indigo, Sodium salicylate, Cr(VI), Hemimellitic, Trimellitic and Pyromellitic acids on the PANi was investigated in a batch system. The adsorption experiments were carried out using a series of glass flasks (250 mL) containing 150 mL of adsorbate solutions and a prefixed amount of adsorbent. The adjustment of pH of the solution was achieved by the addition of HCl and NaOH. The equilibrium concentrations were determined by spectrophotometer (UV 2300) at the maximum absorption wavelength of each adsorbate.

The adsorption efficiency was calculated by the following equation:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

with C_0 and C_e are the initial and equilibrium concentrations (in mg/L), respectively.

3. Results and discussion

3.1. Infrared spectroscopy

3.1.1. Influence of the polymerization time

The FTIR spectra of the PANi formed at different polymerization times are presented in Fig. 2. The analysis of the infrared spectrum at different times allows identifying the major functional groups of the PANi:

- The two bands appearing at 1558.86 cm^{-1} and 1491.93 cm^{-1} are assigned to the vibration of (C=N) bonds of quinoïde cycles and (C–N) of the benzene rings, respectively [23–25]. These two peaks provide qualitative information on the degree of oxidation of PANi [26]. The bands at 1304.75 cm^{-1} and 1245.92 cm^{-1} correspond to the stretching (C–N) of the polymer [27,28]. The most intense peak that appears at approximately 1122.49 cm^{-1} corresponds to the vibration –NH$^+$= which has been formed during the mechanism of protonation [29].
- The bands observed at 750, 780 and 800 cm^{-1} correspond to an aromatic nucleus disubstituted ortho, meta and para, respectively, which indicates that the synthesized PANi has branched structure.

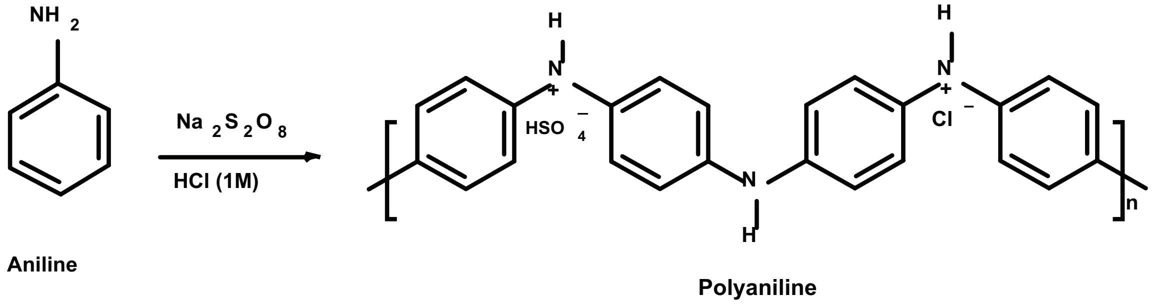

Fig. 1. Oxidative polymerization of aniline monomer by sodium persulfate in HCl solution.

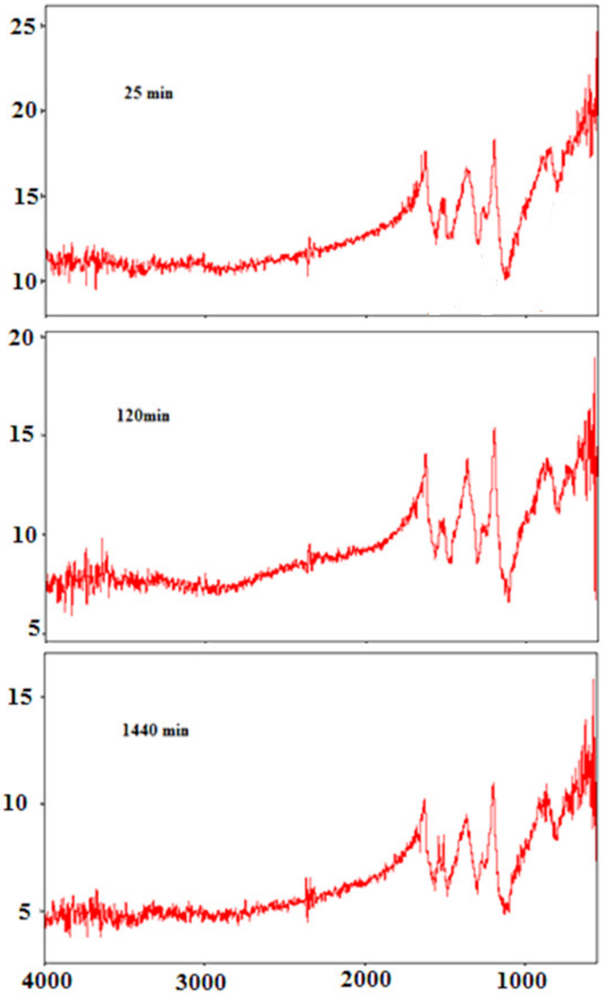

Fig. 2. FTIR spectrum of the PANi at different polymerization times.

According to Fig. 2, the above band characteristics are similar to all spectra. This leads to the conclusion that the polymerization time has no influence on the reaction medium of the polymer.

3.1.2. Influence of the temperature of polymerization

According to the infrared spectra of the PANi obtained at different temperatures 0°C, 25°C and 45°C (Fig. 3). It was observed that the bands characteristics of the PANi are repeated in a typical manner. The variation of temperature during the chemical synthesis of PANi has, therefore, no influence on the appearance/disappearance of functional groups in the final polymer.

3.2. Scanning electron microscopy (SEM)

3.2.1. Effect of polymerization temperature on PANi morphology

The SEM images illustrated in Fig. 4 highlights the effect of temperature on the morphology of the polymer.

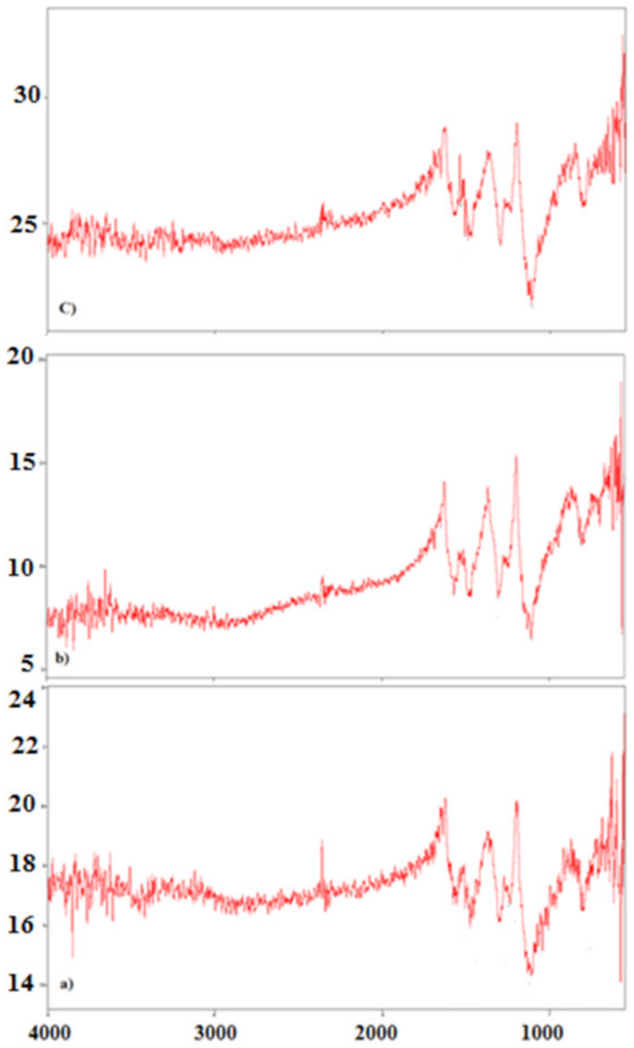

Fig. 3. FTIR spectrum of the PANi at different temperatures: (a) 0°C, (b) 25°C and (c) 45°C.

According to Fig.4, the morphology of the PANi with a drop-by-drop addition of the oxidant is influenced by the increase in the temperature. Specifically, the morphology of the PANi synthesized at 0°C has no obvious distinction, maintaining a homogeneous phase. On the other hand, PANi synthesized at 25°C and 45°C presents the granular and fibril structures, respectively. Furthermore, the porous surface of the PANi may promote the diffusion of pollutants to the internal surface of the PANi as adsorbent material.

3.2.2. Effect of time of polymerization on PANi morphology

The SEM images illustrated in Figs. 5 and 6 highlight the effect of polymerization time on the morphology of PANi depending on the mode of oxidant addition. According to Fig. 5, for a polymerization time of 25 min

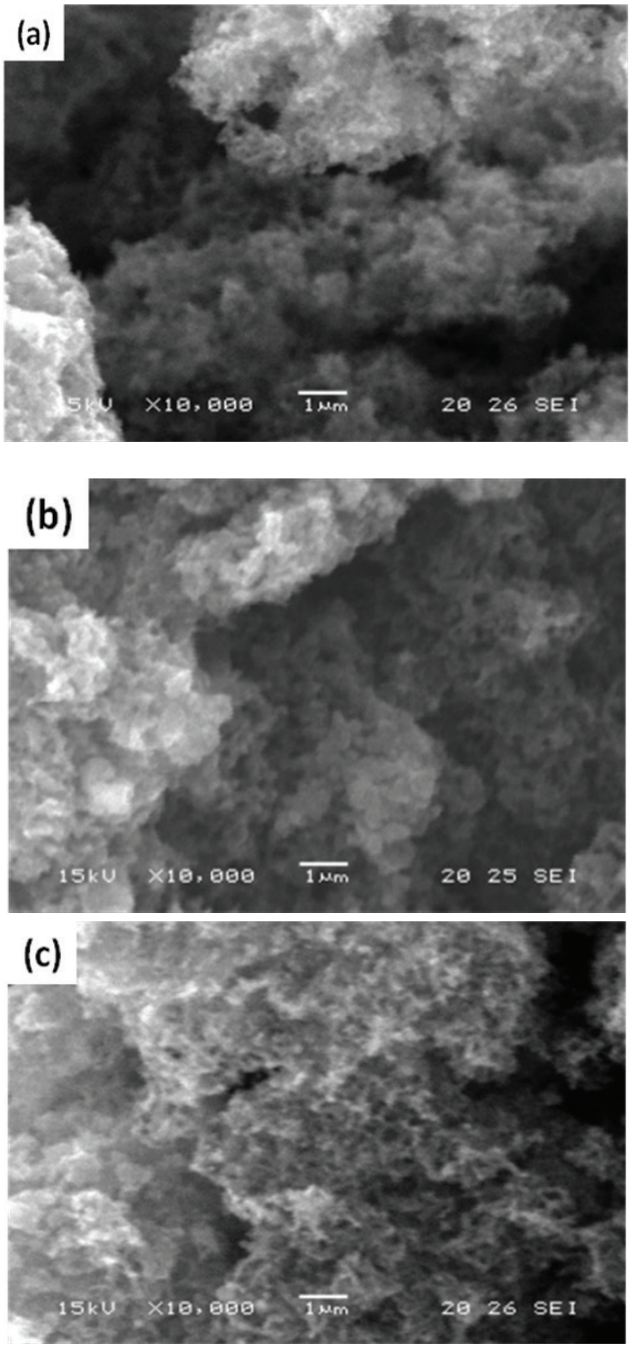

Fig. 4. SEM images of the PANi synthesized at different temperatures: (a) 0°C, (b) 25°C and (c) 45°C.

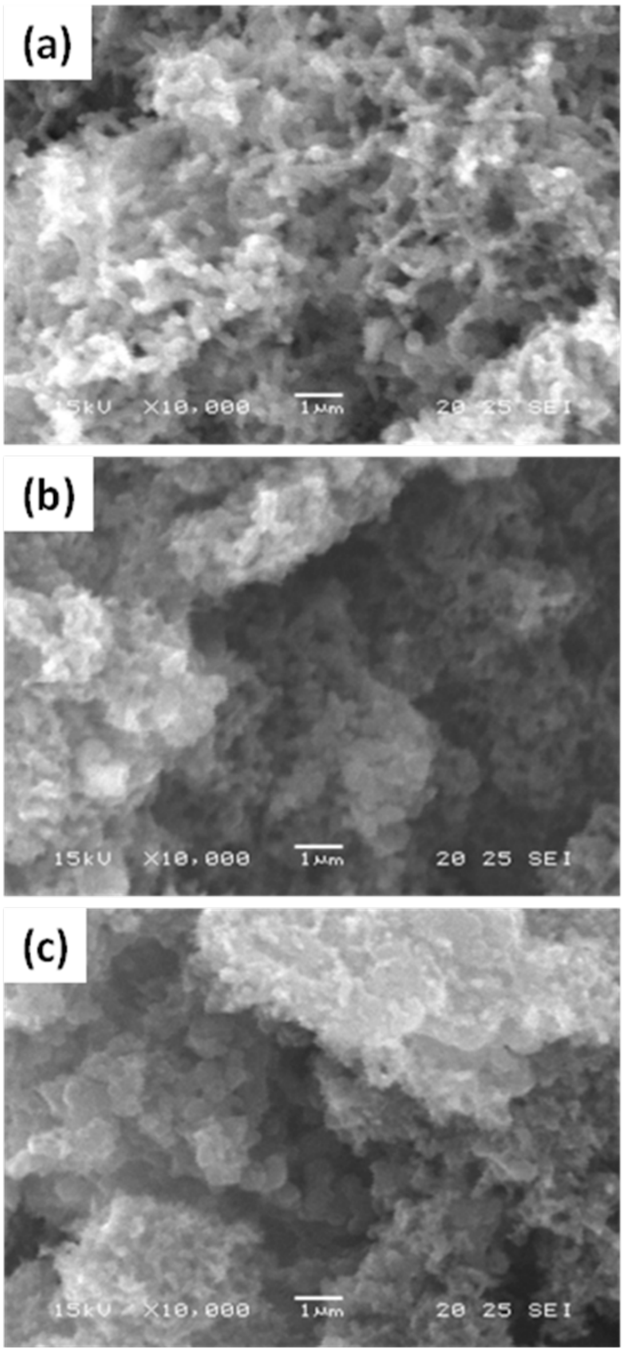

Fig. 5. SEM images of the PANi synthesized at different polymerization times: (a) 25 min, (b) 2 h and (c) 24 h. Addition of oxidant drop-by-drop.

agglomerates are observed in the form of needles or small fibers. In the case of polymerization time of 2 h and 24 h, the agglomerates observed are in the form of grains or platelets. According to Fig. 6, the evolution of the polymerization time by a quick addition of oxidant results to polymers in the form of homogeneous agglomerates.

From Figs. 5 and 6 it is understood that the mode of oxidant addition may significantly affect the morphology of the synthesized PANi. Fig. 5b shows homogeneous agglomerates in the form of toothed platelets. However, Fig. 6b shows agglomerates that are lesser distinct than in the previous case. According to the SEM images obtained for different polymerization times, it is concluded that 2 h of polymerization (Fig. 5b) would be favourable for further studies of pollutants adsorption by the polymer. This is confirmed by the results of the adsorption testing, described below.

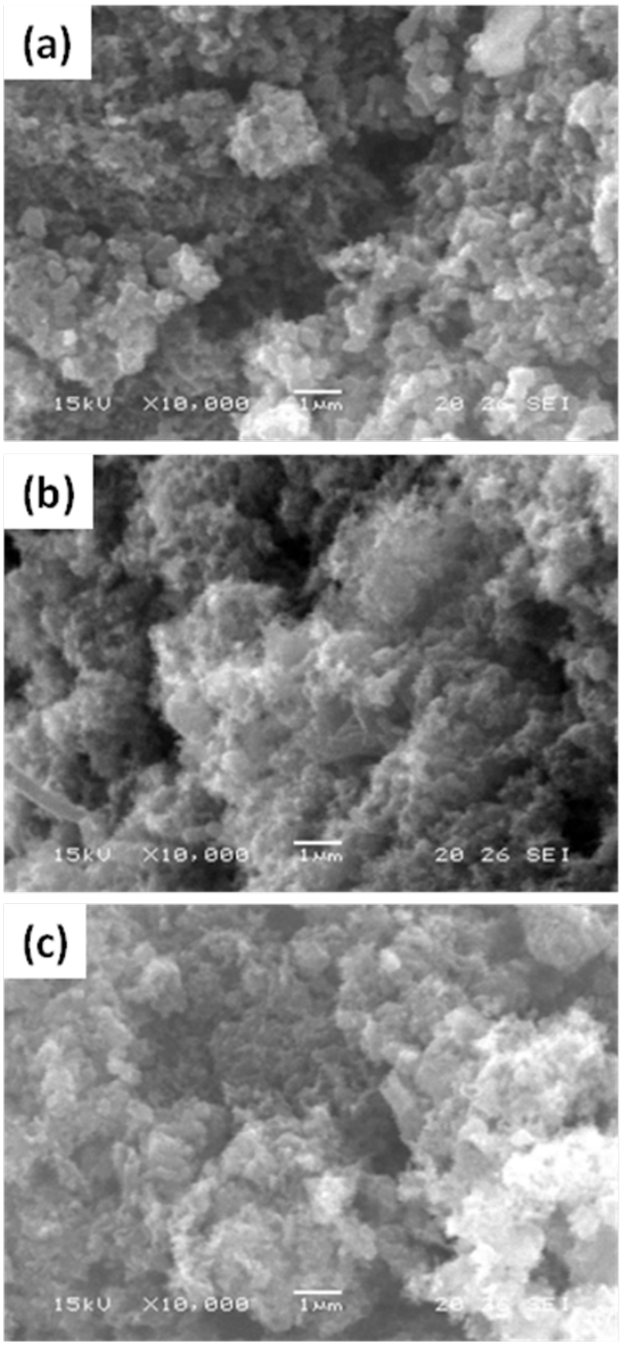

Fig. 6. SEM images of the PANi synthesized at different polymerization times: (a) 25 min; (b) 2 h; (c) 24 h. Rapid addition of oxidant.

3.3. X-ray diffraction (XRD) analysis

The diffraction diagram of the PANi (Fig. 7) consists of four, close and intense peaks, which originate from the ordered zones of the material. The main lines of reflection are present at $2\theta = 8°$; $2\theta = 15°$; $2\theta = 20°$; $2\theta = 25°$, which suggests that the synthesized PANi was in the protonated conducting state (PANi emeraldine-salt form) [30,31]. In addition, the conductive form of PANi is positively charged. This indicates that the PANi can be considered as a suitable adsorbent material for removal of anionic pollutants from wastewater.

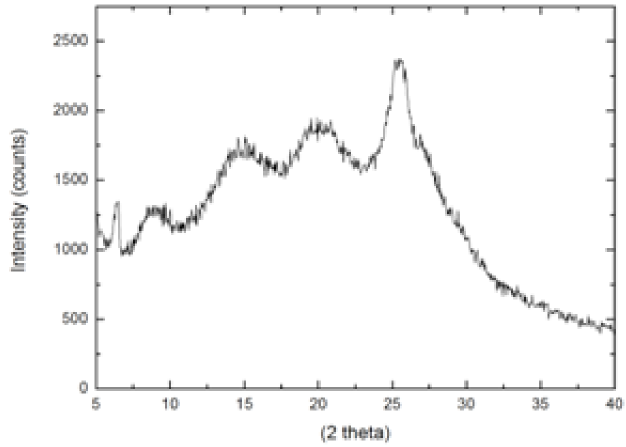

Fig. 7. Diffraction diagram X-ray of the PANi.

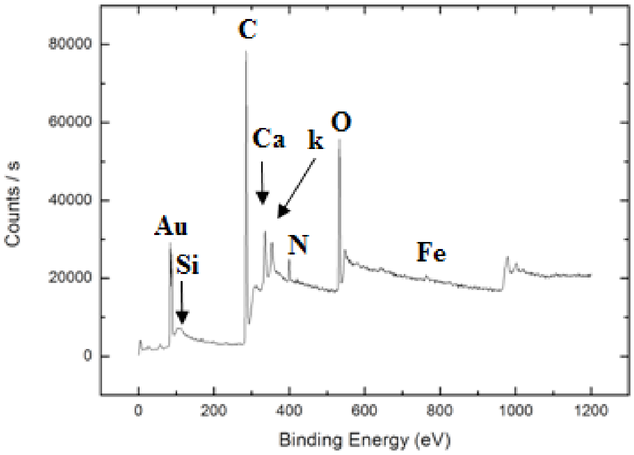

Fig. 8. XPS diagram of the PANi.

3.4. X-ray photoelectron spectroscopy (XPS) analysis of PANi

The XPS analysis of the PANi is presented in Fig. 8. The major peaks observed are Au 4f, C 1s, N 1s, O 1s centred to 85, 285, 400, 529 eV, respectively. The presence of the peaks of the carbon and nitrogen are assigned to the atoms belonging to the polymer. The signal of the oxygen observed at 529 eV is attributed to the oxygen atoms belonging to the hydrogen sulfate counter ions. The peaks of Si, Ca, K, and Fe are impurities of the reagents.

3.5. Thermal analysis of PANi

The results obtained by thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) of 10 mg of PANi are shown in Fig. 9. According to Fig. 9a, a loss of PANi mass is recorded in the area 25–100°C (approximately 11%). This is due to the evaporation of the water. Subsequently, a more significant loss of mass is observed after 400°C, which corresponds to the degradation of the PANi polymer. These results indicate the PANi possesses a good thermal stability.

3.6. Adsorption of pollutants on the PANi

The objective of this section is to examine the ability of the PANi to adsorb various types of pollutants such as Congo red, carmine indigo, sodium salicylate, Cr(VI), hemimellitic, trimellitic and pyromellitic acids from aqueous solutions. The effects of experimental factors such as pH, contact time, initial concentration, and temperature on the adsorption process were systematically investigated. The optimization of experimental parameters for all studied pollutants was carried out using one variable at a time method in a batch adsorption system.

The obtained results in the optimum operating conditions are summarized in Table 1. From these results, it was observed that the removal yield of all studied pollutants by PANi tend toward 100%, which indicates the good affinity of the adsorbates on the surface PANi. This adsorption behavior may be related to the porous structure of the PANi, which facilitates the penetration of adsorbate molecules to interior pores of the adsorbent. In addition, the electrostatic interactions between adsorbate molecules charged negatively and surface of the PANi charged positively may be considered as an important factor involved in the adsorption process of all pollutants on the PANi.

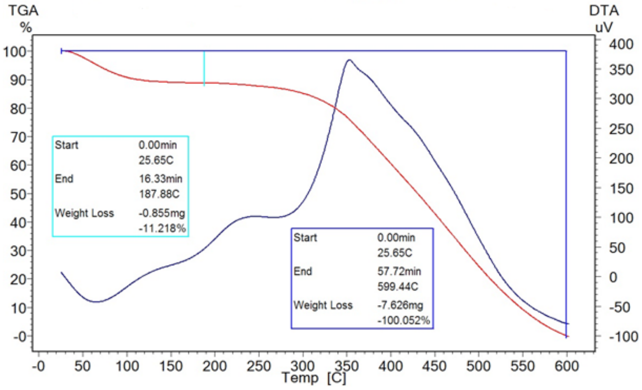

Fig. 9. Thermal treatment of the PANi under air with 10°C/min.

The high removal efficacy of the various studied pollutants indicates that the synthesized PANi can be used as a potential and eco-friendly adsorbent for removal of different types of pollutants from industrial effluents.

4. Conclusion

The chemical oxidation of PANi was carried out in the presence of sodium persulfate in an acidic environment. The effect of different synthesis conditions was examined, and the following conclusions were drawn:

- The results of the infrared spectroscopy show that the polymerization time and temperature have no effect on the polymerization.
- Scanning electron microscopy analysis showed that the morphology of the PANi synthesized at 0°C is not very different form the one obtained at 25°C; though, its morphology at 45°C is in the form of toothed pads and in cauliflower forms.
- The drop by drop addition of the oxidant allows after 25 min of polymerization the synthesis of PANi agglomerates in the form of needles or small fibers.
- Contrarily, the synthesis of the PANi, after 2 h and 24 h of polymerization, resulted to agglomerates in the form of platelets.
- The rapid addition of the oxidant led to the formation of homogeneous PANi agglomerates.
- The X-ray diffraction (XRD) results assign an amorphous structure with the partial order to PANi.
- The peaks of carbon and nitrogen presented in the results of XPS are attributable to the atoms belonging to PANi.
- The results of thermal analysis showed that PANi demonstrates thermal degradation around 400°C.
- The adsorption capacity of the synthesized PANi is independent of the nature of the pollutants, reaching 100% for most of the tested compounds (Dyes, Cr(VI), Humic acid derivatives, Pharmaceutical by-product) under optimal conditions.

References

[1] A. Ray, G.E. Asturias, D.L. Kershner, A.F. Richter, A.G. MacDiarmid, A.J. Epstein, Polyaniline: Doping, structure and derivatives, Synth. Met., 29 (1989)141–150.

Table 1
Optimum experimental conditions and adsorption efficacy for each type of pollutant on the PANi

Pollutant	Adsorbent dose (g/l)	Initial concentration (mg/l)	pH of solution	Contact time (min)	Temperature (°C)	Performance (%)
Congo red	0.40	20	6.55	45	25	100
Carmine Indigo	0.66	10	5.00	45	25	98.27
Sodium salicylate	0.66	10	4.62	60	25	86.31
Cr(VI)	1.00	50	5.00	45	25	98.20
Hemimellitic acid	0.66	10	5.43	60	25	98.95
Trimemillitic acid	0.66	10	5.43	60	25	98.17
Pyromellitic acid	0.20	10	4.40	60	25	97.01

[2] A. Hugot-Le Goff, M.C. Bernard, Protonation and oxidation processes in polyaniline thin films studied by optical multichannel analysis and in situ Raman spectroscopy, Synth. Met., 60 (1993) 115–131.

[3] G. Ćirić-Marjanović, Recent advances in polyaniline research: Polymerization mechanisms, structural aspects, properties and applications, Synth. Met., 177 (2013) 1–47.

[4] M. Eising, C.E. Cavab, R.V. Salvatierra, A.J.G. Zarbin, L.S. Roman, Doping effect on self-assembled films of polyaniline and carbon nanotube applied as ammonia gas sensor, Sens. Actuators, B 245 (2017) 25–33.

[5] Y. Zhao, Z. Zhang, L. Yu, Corrosion protection of carbon steel by electrospun film containing polyaniline microfibers, React. Funct. Polym., 102 (2016) 20–26.

[6] L. Huang, X. Li, Y. Ren, X. Wang, In-situ modified carbon cloth with polyaniline/graphene as anode to enhance performance of microbial fuel cell, Int. J. Hydrogen Energy, 41 (2016) 11369–11379.

[7] M. Laabd, H. Chafai, A. Essekri, M. Elamine, S.A. Al-Muhtaseb, R. Lakhmiri, A. Albourine, Single and multi-component adsorption of aromatic acids using an eco-friendly polyaniline-based biocomposite, Sustain. Mater. Technol., 12 (2017) 35–43.

[8] A. Pron, P. Rannou, Processible conjugated polymers: from organic semiconductors to organic metals and superconductors, Prog. Polym. Sci., 27 (2002) 135–190.

[9] A.G. Green, A.E. Woodhead, Aniline-black and allied compounds. Part I, Chem. Soc., 97 (1910) 2388–2403.

[10] A.G. Green, A.E. Woodhead, Aniline-black and allied compounds. Part II, Chem. Soc., 101 (1912) 1117–1123.

[11] Y. Wei, K.F. Husueh, G.W. Jang, A study of leucoemeraldine and effect of redox reactions on molecular weight of chemically prepared polyaniline, Macromolecules, 27 (1994) 518–525.

[12] Y. Sun, A.G. Macdiarmid, A.J. Epstein, Polyaniline: synthesis and characterization of pernigraniline base, Chem. Soc., Chem. Commun., 7 (1990) 529–531.

[13] H. Chafai, H. Lotfi, M. Bazzaoui, A. Albourine, Adsorption du salicylate de sodium et du Cr(VI) par lepolypyrrole, J. Mater. Environ. Sci., 4 (2013) 285–292.

[14] M. Laabd, H. Ait Ahsaine, A. El Jaouhari, B. Bakiz, M. Bazzaoui, M. Ezahri, A. Albourine, A. Benlhachemi, Congo red removal by PANi/Bi_2WO_6 nanocomposites: Kinetic, equilibrium and thermodynamic studies, J. Environ. Chem. Eng., 4 (2016) 3096–3105.

[15] M. Laabd, N. Aarab, H. Chafai, M. Bazzaoui, M. Elamine, R. Lakhmiri, A. Albourine, Chemical synthesis of polypyrrole film and its adsorption capacity for aromatic polycarboxylic acids, Fibers Polym., 18 (2017) 1064–1072.

[16] V.K. Gupta, I. Ali, T.A. Saleh, A. Nayak, S. Agarwal, Chemical treatment technologies for waste-water recycling-an overview, RSC Adv., 2 (2012) 6380–6388.

[17] W. Yu, N.J.D. Graham, G.D. Fowler, Coagulation and oxidation for controlling ultrafiltration membrane fouling in drinking water treatment: application of ozone at low dose in submerged membrane tank, Water Res., 95 (2016) 1–10.

[18] Z.Y. Zhao, D.J. Gu, H.B. Li, X.Y. Li, K.M.Y. Leung, Disinfection characteristics of the dissolved organic fractions at several stages of a conventional drinking water treatment plant in Southern China, J. Hazard. Mater., 172 (2009) 1093–1099.

[19] A. Assabane, Y. Ait Ichou, H. Tahiri, C. Guillard, J.M. Herrmann, Photocatalytic degradation of polycarboxylic benzoic acids in UV-irradiated aqueous suspensions of titania.: Identification of intermediates and reaction pathway of the photomineralization of trimellitic acid (1,2,4-benzene tricarboxylic acid), Appl. Catal. B Environ., 24 (2000) 71–87.

[20] M. Laabd, A. El Jaouhari, M.d Bazzaoui, A. Albourine, H. El Jazouli, Adsorption of Benzene-Polycarboxylic acids on the electrosynthesized Polyaniline films: experimental and DFT calculation, J. Polym. Environ., 25 (2017) 359–369.

[21] M. Laabd, H. Chafai, N. Aarab, A. El Jaouhari, M. Bazzaoui, H. Kabli, H. Eljazouli, A. Albourine, Polyaniline films for efficient removal of aromatic acids from water, Environ. Chem. Lett., 14 (2016) 395–400.

[22] A.G. MacDiarmid, J.C. Chiang, A.F. Richter, A.J. Epstein, Polyaniline: a new concept in conducting polymers, Synth. Met., 18 (1987) 285–290.

[23] S. Sariciftci, H. Kuzmany, H. Neugebauer, A. Neckel,Structural and electronic transitions in polyaniline: A Fourier transform infrared spectroscopic study, J. Chem. Phys., 92 (1990) 4530–4539.

[24] H. Yan, N. Toshima, Chemical preparation of polyaniline and its derivatives by using cerium(IV) sulfate, Synth. Met., 69 (1995) 151–152.

[25] N. TrinhTung, Y.-J. Yu, K. Kim, S.H. Joo, Y. Park, J.I. Jin, Versatile preparation of poly(1,4-phenylenevinylene-co-1,4-phenylene-1,2-ethanediyl) by CVD polymerization of p-(methoxymethyl)benzylchloride, J. Polym. Sci., Part A: Polym. Chem., 43 (2005) 742–751.

[26] E.T. Kang, K.G. Neoh, T.C. Tan, S.H. Khor, K.L. Tan, structural studies of poly(p-phenyleneamine) and its oxidation, Macromolecules, 23 (1990) 2918–2926.

[27] J. Tang, X. Jing, B. Wang, F. Wang, Infrared spectra of soluble polyaniline, Synth. Met., 24 (1988) 231–238.

[28] T.K. Rout, G. Jha, A.K. Singh, N. Bandyopadhyay, O.N. Mohanty, Development of conducting polyaniline coating: a novel approach to superior corrosion resistance, Surf. Coat. Technol., 167 (2003) 16–24.

[29] J. Stejskal, I. Sapurima, J. Prokes, J. Zemek,In-situ polymerized polyaniline films, Synth. Met., 105 (1999) 195–202.

[30] Z.M. Zhang, Z.X. Wei, M.X. Wan, Nanostructures of polyaniline doped with inorganic acids, Macromolecules, 35 (2002) 5937–5942.

[31] Z. Zhang, M. Wan, Y. Wei, Highly crystalline polyaniline nanostructures doped with dicarboxylic acids, Adv. Funct. Mater., 16 (2006) 1100–1104.