



Plasma polymerization of pyrrole and aniline on polyurethane foams for microorganism immobilization and wastewater treatment

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ABSTRACT

The development of new approaches for wastewater treatment is a current challenge for scientists and technologists. Microorganism immobilization onto supports for wastewater treatment is a powerful tool of low cost and highly efficient. Therefore, in this work pyrrole and aniline were copolymerized on the surface of polyurethane (PU) foams by the plasma polymerization method (changing the power input, atmosphere of reaction, and polymerization time) to obtain polyurethane/polypyrrole/polyaniline (PU/(PPy-co-PANI)) composites which were used as supports for microorganism immobilization and tested in municipal wastewater treatment in anaerobic batch and continuous packed-bed reactors. The supports were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA); chemical oxygen demand (COD) removal efficiency, during the treatment of municipal wastewater, was determined. It was observed from SEM analysis that PPy-co-PANI deposited onto the PU surface can be a homogeneous sheet coating PU or spherical nanostructures with average diameters between 50 nm and 1 µm, depending on the plasma polymerization conditions. Batch wastewater treatment after 48 h showed COD removal efficiencies of 30%, 28%, 26%, 61% and 56% for the PU and PU/(PPy-co-PANI) composites obtained at 40 W and 55 min, 30 W and 45 min, 50 W and 30 min (air plasma first) and, 45 W and 40 min (acrylic acid plasma first), respectively; which was associated to the polymers morphology deposited onto the PU foam surface. The composite of PU/(PPy-co-PANI) obtained at 50 W and 30 min (air plasma first) was tested in the continuous wastewater treatment, observing that for 54 h of hydraulic retention time (HRT), 76% of COD removal can be achieved.

Keywords: Plasma polymerization; Conducting polymers; Immobilization, Biodegradation

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1. Introduction

The World Commission on Water for the twenty-first century presented different water situations in the world by the year 2025, of which in the scenario between 1995 and 2025, the zones affected by severe water demand will expand and intensify, and therefore there will be a strong competition by water resource between industrial, domestic and agriculture uses [1]. Water pollution is usually defined as the addition of substances or energy forms that directly or indirectly affects the nature of the water body in such a manner that negatively affects its legitimate uses [2]. Considering that the wastewater treatment purpose is not the obtaining of pure water ready for drinking but to reduce hazardous microorganism and organic substances until safe concentrations so that water can be used for industrial or agriculture applications, the appropriate choice of wastewater technology has to be made taking into account factors as volume, composition and requirements of water discharges [3]. The biological process is a promising technology for wastewater treatment, and in recent years wide attention has been given towards the development of systems for anaerobic treatment of wastes for the conversion of dissolved and suspended organic contaminants to biomass, CO_2 , CH_4 , N_2 and SO_2 [4,5]. For example, Karimi and Hassanshahian [6] isolated phenol-degrading yeast from the soil and wastewater of a coking plant, they observed up to 95% of phenol biodegradation at relatively low initial concentration. In other work, Hassanshahian and Boroujeni [7] isolated and characterized naphthalene-degrading bacteria from marine samples, observing 89% of naphthalene degradation.

Recently, the microorganism immobilization method has been considered for bioremediation, including wastewater treatment. Immobilization can be defined as limiting the mobility of microorganisms or their enzymes with preservation of their viability and catalytic functions [8–10]; this can be achieved by forming a biofilm on the surface of a synthetic or natural support [11], therefore the physical and chemical properties of support material is of particular importance, specially factors as specific surface area, porosity, the surface homogeneity, and biocompatibility/non-toxicity with the immobilized microorganisms, besides the consideration of low cost, raw materials availability and easy synthesis/preparation [12,13]. By increasing the availability of the substrates for the microorganisms, and a better interaction between substrates and the immobilized cells, synergistically results in an increase of the degradation rate of organic matter [14]. Consequently, a lot of synthetic and modified natural materials have been used as supports, such as celluloses, chitosan, zeolites, anthracite, porous glass, activated char-coal, and ceramics [15], and a variety of synthetic polymers as poly(vinyl alcohol) [16], poly(methyl methacrylate) [17], polypropylene [18], polystyrene [19], PU [20], and modified PU [21].

Polyurethane foam possesses high mechanical strength, resistance to organic solvents and microbial attack and easy handling, therefore is excellent as support for microorganism immobilization [22]. The synthesis of materials of PU with semiconducting polymers obtained by the typical chemical oxidation for different applications (actuators, tissue engineering, electrodes, etc. [23–27]) has been reported.

In a previous work, we reported the modification of PU foams polymerizing pyrrole and aniline onto their surface by chemical oxidization, which were used to immobilize microorganisms for municipal wastewater treatment in batch mode and continuous flow using two sequential (anaerobic/aerobic) packed-bed reactors (PBR) [12]. The most used conducting polymers as polypyrrole or polyaniline can be obtained by electropolymerization, thermal polymerization and chemical oxidative polymerization. The last method is the more common due to its practicality, fast polymerization and because high amounts can be synthesized. However, plasma polymerization method can be useful for homogeneous coating of surfaces.

Plasma polymerization allows the obtaining of polymeric thin layers with adjustable compositions and well-defined nanostructures. When monomers with functional groups are used, it is possible to obtain polymer films with homogeneous functional groups [28]. Polymers obtained by plasma are useful in solid coating such as membranes, metals, textiles and other polymers, achieving layer thicknesses between 10 and 100 nm. The proper monomer choice allows the performance of properties such as corrosion, chemical and abrasion resistances, optical and electrical properties, as well as the biocompatibility in the case of biotechnological applications. It has been reported that in the polymer structure obtained through plasma, unsaturation (double and triple bonds between C atoms) can be formed. Also, polymer cross-linking and oxygen bonding to polymers when exposed to air can be presented. In the case of pyrrole plasma polymerization, hydrolysis of nitrile groups has been suggested due to reaction with water from the environment [29–30].

The aim of this work was the synthesis of PU/ (PPy-co-PANI) composites by plasma polymerization using different plasma conditions such as plasma power input, polymerization time and plasma type (air and acrylic acid) before pyrrole and aniline polymerization in order to obtain the composite surface with the best morphology and physicochemical properties to be used in microorganism immobilization for COD removal during municipal wastewater treatment in anaerobic batch reactors and in continuous flow using an anaerobic packed-bed reactor.

2. Experimental setup

2.1. Materials

Pyrrole (>98%) and aniline (>99%) were purchased from Sigma-Aldrich™ and used as received. Polyurethane foam (PU) was acquired from a local market in Saltillo, Mexico. Distilled grade water was used in all polymerizations. Sulfuric acid (96%–98%) and potassium dichromate (96%–98%) were purchased from Analytika® (Mexico), mercuric sulfate (>98%) and silver sulfate (>98%) from Jalmek-Científica, and potassium biphtalate (>99.95%) from Fermont (Mexico); these reagents were used for COD determinations.

2.2. Plasma polymerizations

Polymerizations of pyrrole and aniline onto PU foams surface were performed as follows: first 10 g of PU foams were

cut in pieces of approximately $1 \times 1 \times 1$ cm and introduced into a cylindrical glass (capacitively coupled) plasma reactor, with a vacuum pump, a radiofrequency power generator (Aja International, RF600A) operated at 13.56 MHz, a matching network (Aja International) and a glass gas trap containing liquid nitrogen to avoid the pass of reactant to the vacuum pump [31]. PU foams were placed inside the cylindrical glass reactor. Outside around the reactor, an electrode copper coil was placed; one of the ends of the coil was connected to the plasma generator. The pressure inside the reactor was fixed at around 1.7×10^{-1} mbar and the monomer mixture (pyrrole to aniline 1:1 v/v) was introduced inside the plasma reactor without the use of a carrier gas. The plasma polymerization conditions are given in Table 1.

2.3. Microorganism immobilization

Domestic wastewater and anaerobic sludge used in biofilm formation onto the supports in this study were obtained from a treatment plant. 500 mL batch glass reactors labeled as shown in Table 1 were used; to which 1 g of support, 10% of anaerobic sludge (v/v), and 40% (v/v) of domestic wastewater as substrate were added. The systems worked batchwise with gently periodical homogenization for 15 d at room temperature under anaerobic conditions for biofilm formation. Afterwards, the supernatant was removed along with the excess of sludge [13].

2.4. Anaerobic batchwise wastewater treatment

Kinetic experiments of COD removal were made at room temperature using reactors containing the supports with immobilized microorganisms (biofilm) with four replicates for each treatment, under anaerobic conditions containing 50% (v/v) of municipal wastewater obtained from the plant "Bosque Urbano Ejército Mexicano" (Saltillo, Mexico). Samples were withdrawn as follows: each reactor was gently stirred to homogenize the contents without damaging the biofilm/foams and allowed to stand for 5 min to settle large solids and tilted slightly to sample the aqueous phase with a hypodermic syringe every 24 h throughout 8 d to determine the COD profile [12].

2.5. Continuous wastewater treatment in a packed-bed reactor

An acrylic tubular reactor of 2.2 L of working volume ($I.D. \times h = 7.5 \times 50$ cm) was used in this study. The reactor operated in anaerobic up-flow mode, in which the

wastewater was fed at the bottom. First, the reactor was packed and conditioned as follows: 720 mL of anaerobic sludge were placed inside the reactor along with 14 g of the PU/(PPy-co-PANI)-50W-30-Air support and then 700 mL of domestic wastewater were recirculated at low rate through the packed supports. The system was allowed to be in contact for 15 d for biofilm formation and attachment on the support. At the end of this period the sludge and wastewater were carefully removed from the reactor, keeping the supports inside the reactor with its biofilm. To assure removal of sludge excess (prior to the test), a sodium acetate aqueous solution and then potable water were passed through the system. Afterwards, municipal wastewater was continuously fed to reactor using a HRT of 54 h. The first sample was collected of the effluent after 54 h of feeding and the following samples were collected every 24 h, for a period of 15 d.

2.6. Characterization

PU foam and PU/(PPy-co-PANI) supports were analyzed by FTIR-ATR spectroscopy (Agilent Tech., Cary 630) to determine chemical composition and by scanning electron microscopy (SEM) (FEI, Quanta-3D FEG) to observe the morphology of the composites surface. Thermal stability of samples was studied by thermogravimetric analysis (TGA550, TA Instrument) using 10 mg of each sample heated from 25°C to 500°C at a rate of 10°C min⁻¹.

COD determinations were made as follows: the aqueous samples were centrifuged by 3 min at 3,000 rpm, using the supernatant to quantify the COD. COD was determined by the closed reflux colorimetric method in accordance with Standard Methods (1995) and NMX-AA-030-SCFI-2012 [32]: 2.5 mL of each sample, standards (potassium biphthalate dilutions) and controls (distilled water) were heated at 150°C in a closed vial (Hach, DRB/200) by 2 h in the presence of acid dichromate solution (3.5 mL of a silver sulphate solution in sulfuric acid and 1.5 mL of potassium dichromate, mercuric sulfate and sulfuric acid solution in distilled water). The samples were then cooled down and their absorbance was measured at 600 nm using a spectrophotometer (HACH, DR/2010).

3. Results and discussion

3.1. Characterization of composites

In plasma polymerization the generated electrons by the electric discharge collides with the monomer molecules

Table 1

Plasma polymerization conditions used in PU foams coating with polypyrrole and polyaniline

Sample	Previous plasma type	Power input (W)	Polymerization time (min)
PU ^a	–	–	–
PU/(PPy-co-PANI)-40W-55	None	40	55
PU/(PPy-co-PANI)-30W-45	None	30	45
PU/(PPy-co-PANI)-50W-30-Air	Air	50	30
PU/(PPy-co-PANI)-45W-40-AAc ^b	Acrylic acid	45	40

^aThis sample corresponds to alone PU as the reference.

^bAA = acrylic acid

producing free radicals and negative ions which polymerize [33]. Therefore, the formed polymer does not contain a well-defined repeating unit, and chains can be branched or cross-linked. In our case, in two of the syntheses PU foams were first exposed to air or acrylic acid plasma with the aim to obtain a PU surface enriched in chemical groups to increase the compatibility with the conducting polymers of pyrrole and aniline and in the application, to perform the microorganism immobilization. Fig. 1(a) shows the FTIR spectra of alone PU and composites obtained through plasma polymerization, Fig. 1(b) is a zoom in the range of 600–1,800 cm^{-1} of the same spectra. Signals at 3,300 and 1,636 cm^{-1} correspond to amine groups ($-\text{NH}$) present in PU foam and, in the aniline and pyrrole units, therefore these signals can easily observed in all spectra. Signal near to 2,970 cm^{-1} belongs to asymmetric aliphatic C–H stretching of sp^3 CH_3 and sp^3 CH_2 groups (alkyl groups). CH_2 groups are present in the PU backbone structure but, as proposed by Morales et al. [34], alkyl groups can also be originated from some broken aniline and pyrrole rings due to plasma ionization not only of monomers but also of polymer chains. Sample exposed first to acrylic acid plasma showed an intense signal around 1,714 cm^{-1} which corresponds to carboxylic acid groups ($\text{C}=\text{O}$), this group is also present in the PU, but its signal is shifted to 1,720 cm^{-1} demonstrating its polymerization and incorporation to this composite. The band at 1,590 cm^{-1} is due to C=C from the aromatic ring. The signal at 1,222 cm^{-1} is ascribed to C–O, and the peak at 1,086 cm^{-1} can be assigned to C–O–C of PU. The most important signals of PANI are: at 811 cm^{-1} due to C–H

aromatic out-of-plane bending of 1,4-ring, at 1,292 cm^{-1} from C–N stretching; and at 1,500 cm^{-1} ascribed to C=C stretching from B rings. Signals of PPy are near to 1,448 cm^{-1} (from C–C ring stretching), and at 1,540 cm^{-1} (from C=C backbone stretching); all these signals overlap with those corresponding to PU.

Fig. 2 shows the SEM images of PU foam, PU/(PPy-co-PANI)-40W-55 and PU/(PPy-co-PANI)-30W-45 supports obtained through plasma polymerization at different magnifications. Whereas Fig. 3 shows the corresponding images of PU/(PPy-co-PANI)-50W-30-Air and PU/(PPy-co-PANI)-45W-40-AAc composites. As expected, a homogeneous surface with average pore diameter of 500 μm (Fig. 2(a)) was observed for alone PU foam. Upon plasma copolymerization of pyrrole and aniline, not only a layer of this copolymer can be observed for the composite obtained at high power input and polymerization time (40 W and 55 min), but also particle agglomeration of 5 μm of size consisting of spherical particles with diameters in the range of 500 nm to 1 μm (Fig. 2(b)). By decreasing the power input of plasma and polymerization time to 30 W and 45 min, respectively, the particle agglomeration is not present and only spherical particles were formed on the semiconducting layer with sizes in the interval from 100 to 500 nm. The layer thickness in this case was approximately 250 nm. When increasing the power of plasma and using low polymerization time but exposing first the PU foam to air plasma, only the polymeric semiconducting layer was obtained (Fig. 3(a)), which can be due to a better interaction between the PU and copolymer of pyrrole and aniline. If PU foams are first exposed to acrylic acid plasma (45 W and 40 min), similar results to those obtained for polymerization with 40 W and 55 min were observed. These results are comparable to those previously reported for similar polymerizations. For example, Paosawatyanong et al. [35] studied the AC plasma polymerization of pyrrole under different plasma power input (they reported the voltage operation of plasma) and observed relatively homogeneous polymer films of thickness between 300 nm to 2.7 μm , depending on the plasma power. L. Zhou et al. [36] obtained polyaniline films through RF plasma polymerization with thickness between 1 and 2 μm , observing in some cases the formation of some spherical particles on the surface of film. On the other hand, Morales et al. [34] copolymerized different ratios of pyrrole to aniline through plasma polymerization; they observed spherical agglomerates with sizes in the range of 0.2–0.4 μm .

Fig. 4(a) shows the thermogravimetric analysis of PU foam and composites obtained through plasma polymerization. An improvement of thermal stability is observed after the semiconducting polymers were attached to PU through plasma polymerization except for the composite obtained at higher plasma power input (50 W and 30 min) and exposed first to air plasma. As can be seen from the derivative of TGA (Fig. 4(b)), PU foam presented two thermal transitions at 296°C which is ascribed to the breaking of urethane bonds (isocyanate groups) and at 375°C which is due to ester decomposition from polyol segments; upon plasma polymerization, the first change shifted to lower temperatures (until 280°C depending on the plasma polymerization condition), while the second thermal change moved to higher temperatures near to 400°C, with the exception of composite obtained by exposing first

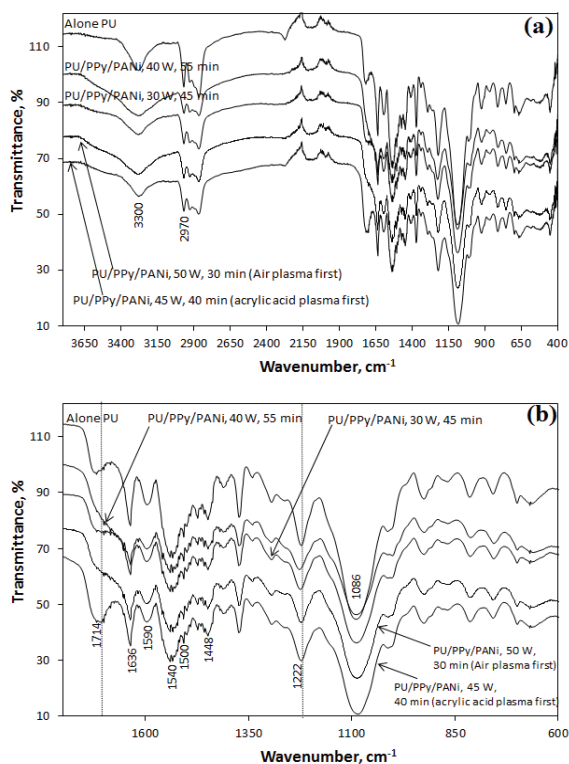


Fig. 1. (a) Full FTIR spectra of alone PU and composites obtained through plasma polymerization, (b) zoom in the range of 600–1,800 cm^{-1} of the same spectra.

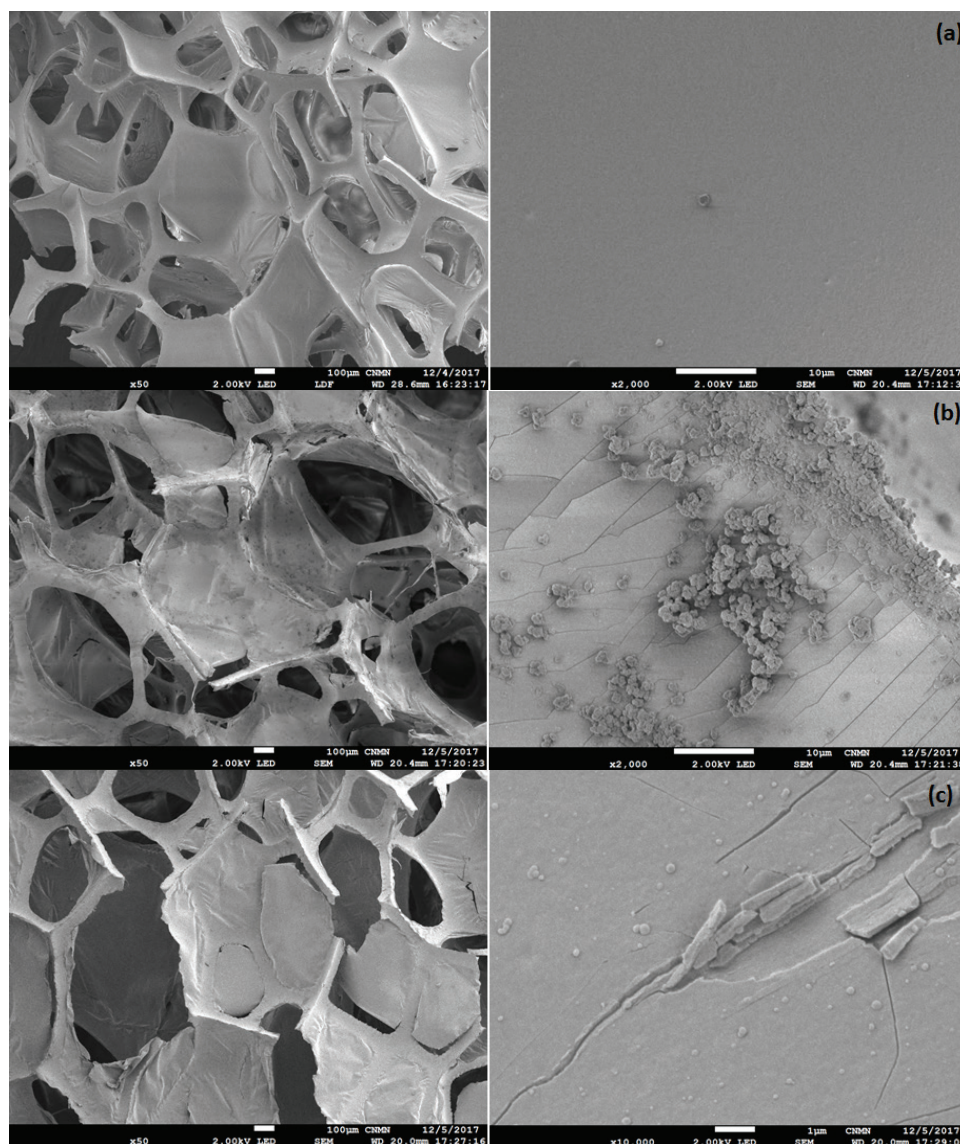


Fig. 2. SEM images of (a) PU foam, (b) PU/(PPy-co-PANI)-40W-55 and (c) PU/(PPy-co-PANI)-30W-45 supports obtained through plasma polymerization at different magnifications.

to air plasma where this second thermal change moved to a temperature of 337°C. As previously reported it is possible that conducting polymers of pyrrole and aniline reduce PU chains mobility slowing the degradation process [12,36].

3.2. Performance of supports in batch wastewater treatment

The modification of surface morphology and chemical composition (double and triple bonds between C atoms, cross-linking and oxygen bonding to polymers when exposed to air, and hydrolysis of nitrile groups) of PU foam by deposition of conducting polymers through plasma polymerization, can imply that more microorganisms and organic molecules can have access to the modified surface, and that positively charged conducting polymers improves adhesion of negatively charged bacteria to the surface through electrostatic attraction [12]. Fig. 5 shows the COD removal at different times of wastewater treatment using the

different supports of PU and composites after microorganism immobilization. Similar COD removal efficiencies can be observed at long times of batch wastewater treatment for all the supports, however at 48 h of degradation, the COD removal efficiency ranged between 26.5% for the composite of PU/(PPy-co-PANI)-30W-45 and 60.9 % for PU/(PPy-co-PANI)-50W-30-Air (Fig. 5(b)). Notwithstanding that the final efficiencies after 192 h of treatment were similar for all the studied composites; the novelty of the present work is the observed efficiency after relatively short biodegradation time using real municipal wastewater. The COD removal efficiency at short times is of importance because these are typical values of hydraulic retention time (HRT) in continuous flow. The observed results imply that conducting copolymers of PPy and PANI offer not only electrical property stimulating microorganism immobilization, but also, the modified morphology and chemical composition of the PU surface affected COD removal efficiency.

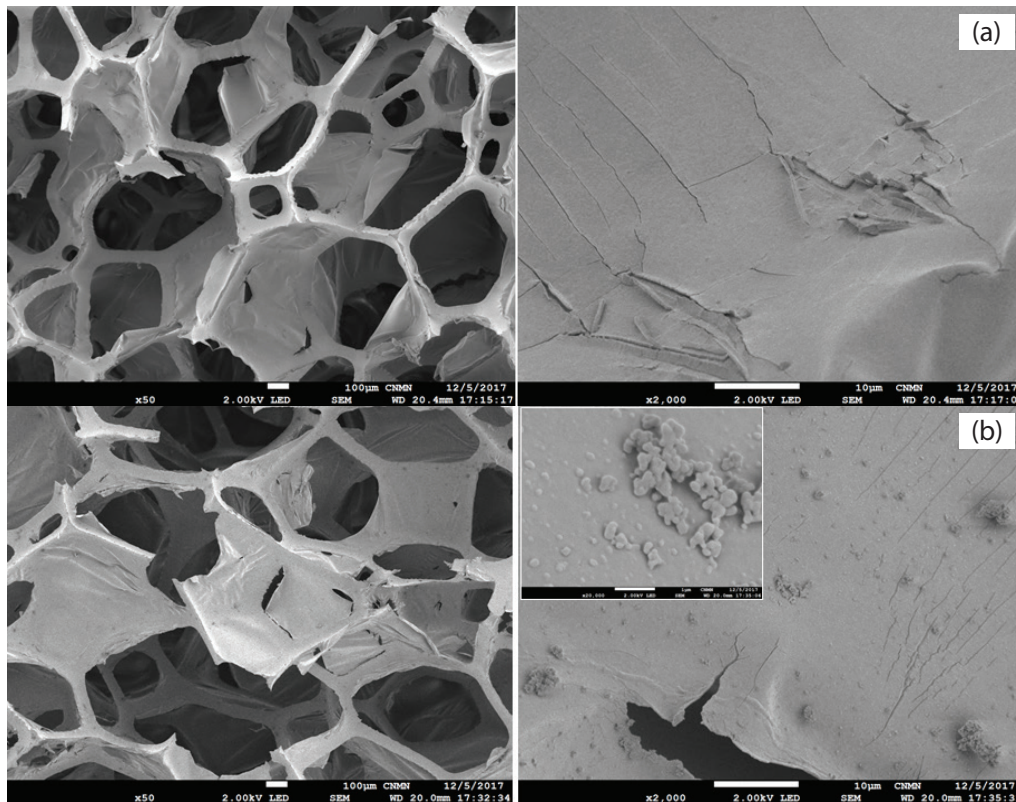


Fig. 3. SEM images of (a) PU/(PPy-co-PANI)-50W-30-Air and (b) PU/(PPy-co-PANI)-45W-40-AAc supports obtained through plasma polymerization at different magnifications.

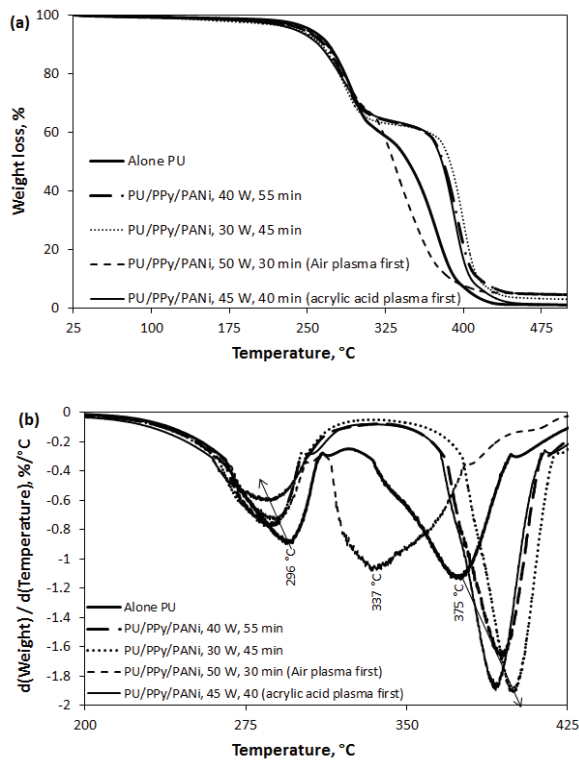


Fig. 4. Thermogravimetric analysis (a) and its derivative (b) of PU foam and PU/(PPy-co-PANI) composites.

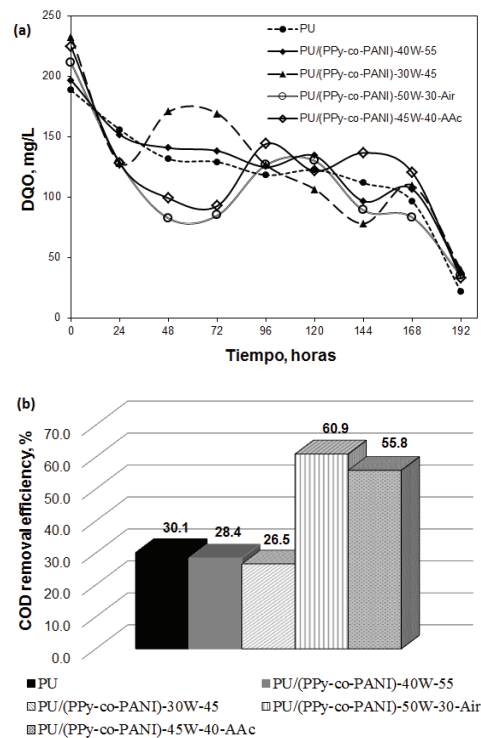


Fig. 5. (a) Batch COD removal profiles as a function of time using the synthesized PU foam supports and (b) efficiency % at 48 h of wastewater treatment.

3.3. Performance of supports in continuous flow in PBR wastewater treatment

According to the results observed in batch mode, the PU/(PPy-co-PANI)-50W-30-Air support was used to immobilize microorganisms in a continuous flow in PBR wastewater treatment in anaerobic conditions. Fig. 6 shows the pH, temperature and COD profiles during wastewater treatment using a HRT of 54 h under steady-state operation in continuous flow in the PBR. It can be observed that pH and temperature remained very stable during the experiments, pH ranged between 7.6 and 8.3 with an average value of 8.0, while temperature oscillated between 20°C and 26°C. Also, the COD removal efficiency increased linearly in the first three days until approximately 65% and then remained very stable in the interval of 56% to 76% of removal efficiency after 15 d of treatment. In our previous work using PU foam coated with PPy and PANI by the typical chemical oxidation of monomers [12], we observed that COD of

the influent strongly influenced the PBR performance, for example for a PBR under anaerobic conditions and using 24 h of HRT, an influent with 366 mg L⁻¹ of COD resulted in a removal efficiency of 40%, whereas for the same conditions but with 676 g L⁻¹ of initial COD the removal efficiency increased until 58%. In the present work the initial COD of wastewater was only 286 mg L⁻¹ achieving average removal efficiencies of 60%, demonstrating that plasma polymerization affected the support performance, of course using higher HRT.

It is difficult to compare the observed results on COD removal efficiency with information in the literature due to the different HRT and operation conditions used in the experiments. Furthermore, in some cases, synthetic wastewaters and isolated microorganisms are tested. Table 2 shows some similar works to the ones here reported. As can be observed, COD removal efficiencies as high as 94.8% can be achieved but at the expense of using more complex wastewater treatment systems, increasing operating costs.

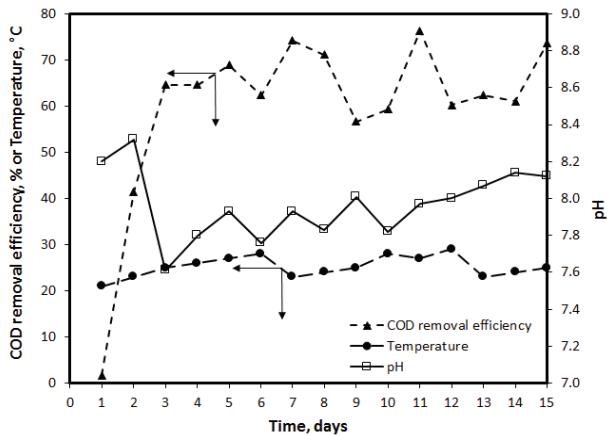


Fig. 6. COD removal efficiency, pH and temperature profiles during wastewater treatment in continuous flow using the PU/(PPy-co-PANI)-50W-30-Air composite as support.

4. Conclusions

Composites of polyurethane/polypyrrole/polyaniline were obtained through plasma polymerization under different conditions and used as supports for microorganism immobilization for municipal wastewater treatment in anaerobic batch and continuous packed-bed reactors. Homogeneous sheet and spherical nanostructures of PPy-co-PANI coating PU can be obtained through this polymerization method, depending on the plasma polymerization conditions. The composite with the best COD removal efficiency during the batch wastewater treatment at 48 h was that obtained at 50 W and 30 min (air plasma first); which was associated to the polymers morphology deposited onto the PU foam surface. It was observed that in the continuous wastewater treatment at 54 h of hydraulic retention time, 76% of COD removal can be achieved.

Table 2

Comparison of different supports reported in literature used for microorganism immobilization in the COD removal during wastewater treatment

Support	Wastewater source	Operation conditions	COD removal efficiency (%)		Reference
			Anaerobic section	Global	
Plastic ring and synthetic fiber string	Coke plant wastewater	Anaerobic-anoxic-oxic in continuous flow	17	92	[37]
Granular activated carbon from coconut	Recycled paper plant	Aerobic in continuous flow	94.8	94.8	[38]
Alginate beads	Synthetic wastewater	Anaerobic in continuous flow with different isolated bacteria	74–95	74–95	[39]
Reticulated sintered glass (Siran ®)	Real textile wastewater	Anaerobic in continuous flow (two sequential reactors)	8–40	8–40	[40]
PU/(PPy-co-PANI)-50W-30-Air	Municipal	Anaerobic in continuous flow	76	76	This work

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