Semiconducting polyurethane/polypyrrole/polyaniline for microorganism immobilization and wastewater treatment in anaerobic/aerobic sequential packed bed reactors

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ABSTRACT: The development of new materials for microorganism immobilization is very important in wastewater treatment. In this work polyurethane (PU) foams were modified polymerizing pyrrole and aniline onto their surface by chemical oxidization to obtain polyurethane/polypyrrole (PU/PPy), polyurethane/polyaniline (PU/PANI), and PU/(PPy-*co*-PANI) supports 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) varying the total hydraulic retention time (HRT). The supports were characterized by Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM) and tested in chemical oxygen demand (COD) removal during treatment of a municipal wastewater. It was observed from SEM analysis that globular nanostructures of PPy and PPy-*co*-PANI were formed onto the PU surface with average diameters between 100 and 300 nm, which are typical of aqueous polymerization of pyrrole monomer; however irregular nanostructures were observed when PANI was homopolymerized onto the PU foam. Batch wastewater treatment after 14 days showed COD removal efficiencies of 77%, 69%, 78%, and 80% for PU foam, PU/PPy, PU/PANI, and PU/(PPy-co-PANI), respectively; which was explained as a function of polymers morphology deposited onto the PU foam surface. Also it was observed from the sequential PBR that for 24 h and 36 h of HRT, 80 and 90% of COD removal can be achieved; respectively.© 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42242.

INTRODUCTION

Water is an absolute requirement for life. On our planet the most controlling resource is water, not oil or minerals. Its distribution, quantity, availability, and quality are the requirements for the development of agriculture or industry and dictate its rural, urban, and municipal use. The water-rich areas of the world are truly the richest places on Earth.[1] Over the last century, the population growth and industrialization have resulted in the pollution of several ecosystems on which human life relies on. In the case of ocean and river quality, such pollution is primarily caused by discharge of inadequately treated

industrial and municipal wastewaters. At the initial discharge, these wastewaters can contain high levels of organic/inorganic pollutants, which can be easily biodegradable, whose impact load on the ecosystems either as Total Suspended Solids (TSS), Biochemical Oxygen Demand (BOD), or Chemical Oxygen Demand (COD), may be in the tens of thousands of mg/L.[2,3] In the treatment of wastewater, the biological process appears to be a promising technology; therefore, in recent years considerable attention has been given towards the development of reactors for anaerobic treatment of wastes leading to the conversion of organic molecules into biogas.[4] The activated sludge process

employed for municipal wastewater treatment uses as much as 30% of the energy consumption in a wastewater treatment plant, most of which goes into aeration. On the other hand, anaerobic processes require no aeration and generate a minimum of excess sludge.[5,6]

One way to improve anaerobic processes is microorganism immobilization onto solid supports. The microorganism immobilization technique is a powerful tool having very important industrial and research applications. Immobilization of any biosystem will depend on the type of bioactive material to be immobilized. The attachment of the active agent to a polymer matrix depends on the physical relationship between support and ligand. However, in biosystems immobilization, the factors that influence the choice of the method to be used are generally empirical.[7] Particularly, a lot of synthetic materials such as poly(vinyl alcohol),[8–11] poly(methyl methacrylate),[12] polypropylene,[13] polystyrene,[14] PU,[15–18] and modified PU[19–21] have been used. As of now, polyurethanes (PU) are one of the most versatile materials in the world. They are known as a perfect material for footwear, machinery industry, coatings and paints, rigid insulation, elastic fiber, soft flexible foams, and medical devices. The immobilization of cells on polyurethane foam offers several advantages including high mechanical strength, resistance to organic solvents and microbial attack, easy handling, regenerability, and cost-effectiveness.[22] It has been found to be applicable in the biochemical and biotechnological fields as a perfect support for enzyme immobilization.[23,24]

The synthesis of materials of PU with semiconducting polymers has been reported. For example, Choi et al.[25] reported the synthesis of PU and deposition of PPy by chemical oxidation of pyrrole monomer onto its surface to be used as actuators. Broda et al.[26] obtained conducting materials of PPy nanoparticles and PU for tissue engineering, from the cytocompatibility assay data they observed no significant cytotoxic effect of the materials. Chiu et al.[27] electrochemically polymerized pyrrole in a matrix of PU. Using this technique, it was observed that PPy grew in a treelike structure with molecular chains extending from the electrode surface into the solution. Also, the transition temperature of the PPy/PU increased with the PPy content. On the other hand, PU has also been coated/mixed with polyaniline (PANI). Bouanga et al.[28] studied the dielectric and electrical properties of PU/PANI material synthesized by chemical oxidation of aniline inside a previously swelled PU film. They observed a relaxation process of the material explained in terms of interfacial polarization due to the double-layer structure of the material film. Rangel-Vazquez et al.[29] synthesized and characterized a copolymer of PU and PANI, they obtained in fact interpenetrated networks by interconnection of the two polymers via condensation of PU prepolymer terminal NCO groups with the amine groups of PANI. These authors proposed a morphological interpretation in which PANI chains formed a phase dispersed in a PU matrix, linked together by an interphase that could be responsible for the connectivity between the two polymers promoting excellent mechanical properties.

In this work, supports of PU/PPy, PU/PANI, and PU/(PPy-co-PANI) were obtained by chemical oxidation of pyrrole and aniline monomers. These supports were used for microorganism immobilization and tested in wastewater treatment. The supports were compared against the COD removal obtained during municipal wastewater treatment in anaerobic batch reactors and in continuous flow using two sequential (anaerobic/aerobic) packed bed reactors. To the best of our knowledge, this is the first time that supports of PU with semiconducting PPy and PANI are used for microorganism immobilization in wastewater treatment.

EXPERIMENTAL

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

Polymerizations
Polymerizations of pyrrole and polyaniline onto PU foam surface were performed as follows: 5 g of PU were cut in pieces of approximately 1 cm × 1 cm × 1 cm and immersed in 500 g of distilled water containing 0.5 g of pyrrole or aniline (in the case of copolymerizations of pyrrole with aniline a molar ratio of these monomers was used) previously dissolved. Entrapped air bubbles were extracted from PU foams and allowed to saturate through 2 h under magnetic stirring. Afterwards a molar amount of APS, with respect to the monomers, as the oxidizing agent was added to the reaction mixture to start polymerization. The reaction proceeded for 5 h looking to achieve high monomers conversions. Coated PU foams were washed several times with distilled water to remove unreacted chemicals and dried in an oven at 60°C for 48 h until reaching constant weight. The amount of polymer incorporation to the PU foam was determined by gravimetry from a mass balance as $CP = (W_f - W_i)/W_f \times 100$, where CP represents the % of conducting polymer in the material of PU/conducting polymer, W_f is the final dried weight of foam after polymerization of pyrrole or aniline, and W_i is the initial dried weight of PU foam.

Microorganism Immobilization onto Supports
Municipal wastewater used in this study was obtained from "Bosque Urbano Ejército Mexicano" (Saltillo, Coah., Mexico). Five hundred millilitres batch glass reactors labeled as PU, PU/PPy, PU/PANI, and PU/(PPy-co-PANI) were used; to which 900 mg of support, 20% of degranulated anaerobic sludge (v/v), and 40% (v/v) of municipal wastewater as substrate were added. The systems worked batchwise for 1 month at 37°C under anaerobic conditions for biofilm formation. Afterwards, the supernatant was removed along with the excess of sludge.

Batch Anaerobic Wastewater Treatment
Kinetic experiments of COD removal were conducted at 37°C using reactors containing supports with immobilized microorganisms (biofilm) with three replicates for each treatment, under anaerobic conditions containing 40% (v/v) of municipal
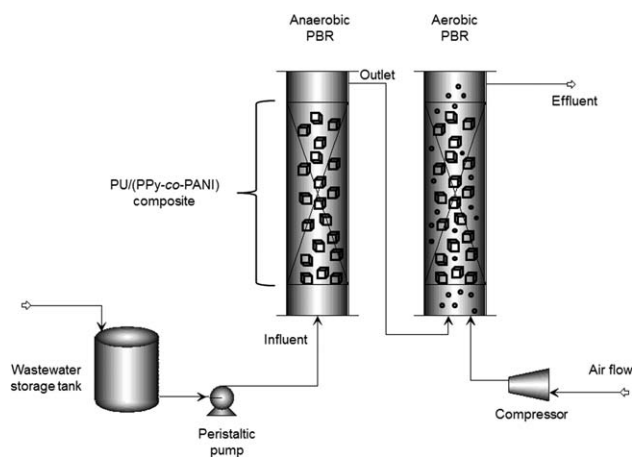
Figure 1. Flowsheet of pilot plant for municipal wastewater treatment with sequential PBR reactors.

wastewater. 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 48 h throughout 15 days to determine the COD.

Continuous Flow Wastewater Treatment in PBR

The pilot plant consisted of two sequential PBR, each having 5.8 L of working volume, packed with 20% wt/v of PU/(PPy-co-PANI) support as shown in Figure 1. The first reactor consisted of an anaerobic up-flow process, in which the wastewater was fed. The output of this reactor was connected to another up-flow aerobic reactor which was connected to an air pump at the bottom for air injection. Each reactor was packed with the PU/(PPy-co-PANI) support used and conditioned as follows: for the anaerobic reactor, 4 L of anaerobic sludge were placed inside the reactor along with the support and a peristaltic pump was connected to recirculate 15 L of municipal wastewater as substrate (12 h oh HRT); whereas for the aerobic reactor, 4 L of aerobic sludge were placed inside the reactor along with the support and a peristaltic pump was connected to recirculate 15 L of municipal wastewater as substrate; in this case, a 4 L air pump was connected at the bottom of the reactor to provide air (12 h of HRT). This process was carried out for 7 days for biofilm attachment on the support. At the end of this period, the sludges and wastewater were carefully removed from each reactor, keeping the supports inside the reactors with their respective biofilms. To assure removal of sludge excess (prior to the tests), municipal wastewater was treated using the system as a sequential PBR for 15 days. Afterwards, a sample of the final effluent from each HRT was collected and analysed.

Characterization

Supports of PU foam, PU/PPy, PU/PANI, and PU/(PPy-co-PANI) were analyzed by FTIR-ATR spectroscopy (Agilent Tech., Cary 630) to determine chemical compositions and by scanning electron microscopy (SEM) (FEI, Quanta-3D FEG) to observe surface morphology. The electrical conductivity of samples was determined by the four-probe method (SP4 probe head

Lucas/Signatone with 0.04 in. of spacing between tips) coupled to a Keithley (2400 SourceMeter) instrument. Samples were powdered and compressed in the shape of disks (1 cm of diameter $\times$ 3 mm of thickness) with 3 tons of pressure. Thermal stability of PU/(PPy-co-PANI) composite and pure PU foam was studied by thermogravimetric analysis (TA Instruments, Q500), 10 mg of each sample was heated between 25 and 400°C at a heating rate of 10°C/min.

The determinations of COD removal during anaerobic wastewater treatment were performed as follows: The aqueous samples were centrifuged (SolbatJ-600 Centrifuge) at 3000 rpm for 3 min before testing, using the supernatant to quantify the COD. Soluble COD was measured by the closed reflux colorimetric method in accordance with Standard Methods (1995) and NMX-AA-030-SCFI-2001[30,31] as follows: 2.5 mL of samples, standards (potassium biphtalate dilutions) and controls (distilled water) were heated at 150°C $\pm$ 2°C in a closed reactor (Hach, Digital Reactor Block 200) for 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 HACH Spectrophotometer (DR 5000).

To establish the amount of biomass attached to the supports, assessments were carried out as follows: A sample of support elements (PU or PU/(PPy-co-PANI)) was weighted and conditioned with 200 mL of sludge (anaerobic and aerobic) and 200 mL of wastewater (as substrate) on a 500 mL batch reactor for 2 weeks. Afterwards, the supports were removed from the reactors, dried at 105°C for 24 h and weighted. This value was compared with the weight of the support before the test, obtaining the biomass weight per gram of support.

RESULTS AND DISCUSSION

Synthesis and Characterization of Supports

Conductive polymers with conjugated double bonds have received great attention as conductive materials. Particularly the interest in polypyrrole (PPy) has grown due to its good environmental stability, ease synthesis, and high electrical conductivity.[32] On the other hand, PANI is a polyaromatic amine that can be easily synthesized from bronsted acidic aqueous solutions. It is one of the most potentially useful conducting polymers and has also received considerable attention in recent years.[33] Figure 2 shows the chemical structure of PPy and PANI bearing positive charges. Both polymers can be prepared by chemical oxidation of the respective monomers or by electrochemical polymerization methods. Many factors can affect their properties such as the method of synthesis and polymerization rate, solvent nature, as well as the pH of the reaction media.[34] The chemical polymerization method is particularly important because this route is more feasible for large-scale production.[35] In this work, conductivity of the as synthesized supports were $<10^{-15}$ S/cm, 7.3×10^{-9} S/cm, 7.4×10^{-10} S/cm, and 7.7×10^{-10} S/cm for PU foam, PU/PPy, PU/PANI, and PU/(PPy-co-PANI), respectively; showing the correct incorporation of conducting polymers to the insulating PU foam.
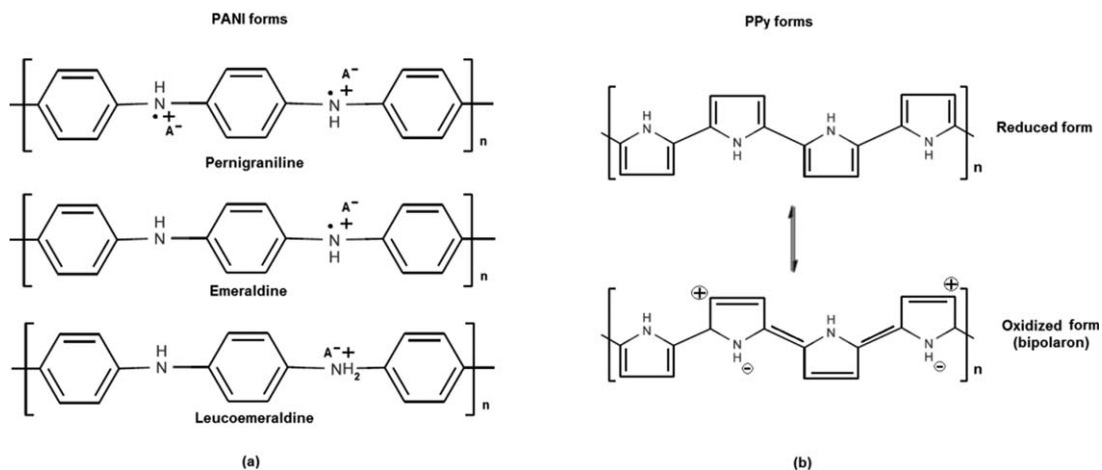
Figure 2. Possible chemical structures of PANI (a) and PPy (b).

Figure 3 shows the SEM images (×33) of different supports synthesized in this work. It can be seen that the PU foam consisted of a homogeneous surface of well-defined pores with average diameter of 500 μm. The sample of PU/PPy showed occluded pores with PPy, while the sample of PU/PANI shows less occluded pores than PU/PPy, and the PU/(PPy-co-PANI) sample showed pores slightly occluded; thus the copolymer of PPy and PANI was deposited only on the surface of PU. As can be seen in Figure 4, a magnification of 10,000 times, the PU foam had a clean uniform surface (a) and upon polymer coating a very heterogeneous surface resulted. PPy formed spherical agglomerated structures with diameters between 300 and 650 nm, which are typical of PPy formation in aqueous dispersion without the presence of any surfactants. PANI formation onto the PU foam surface resulted in polymer agglomerates of irregular morphology and sizes of approximately 300 nm.
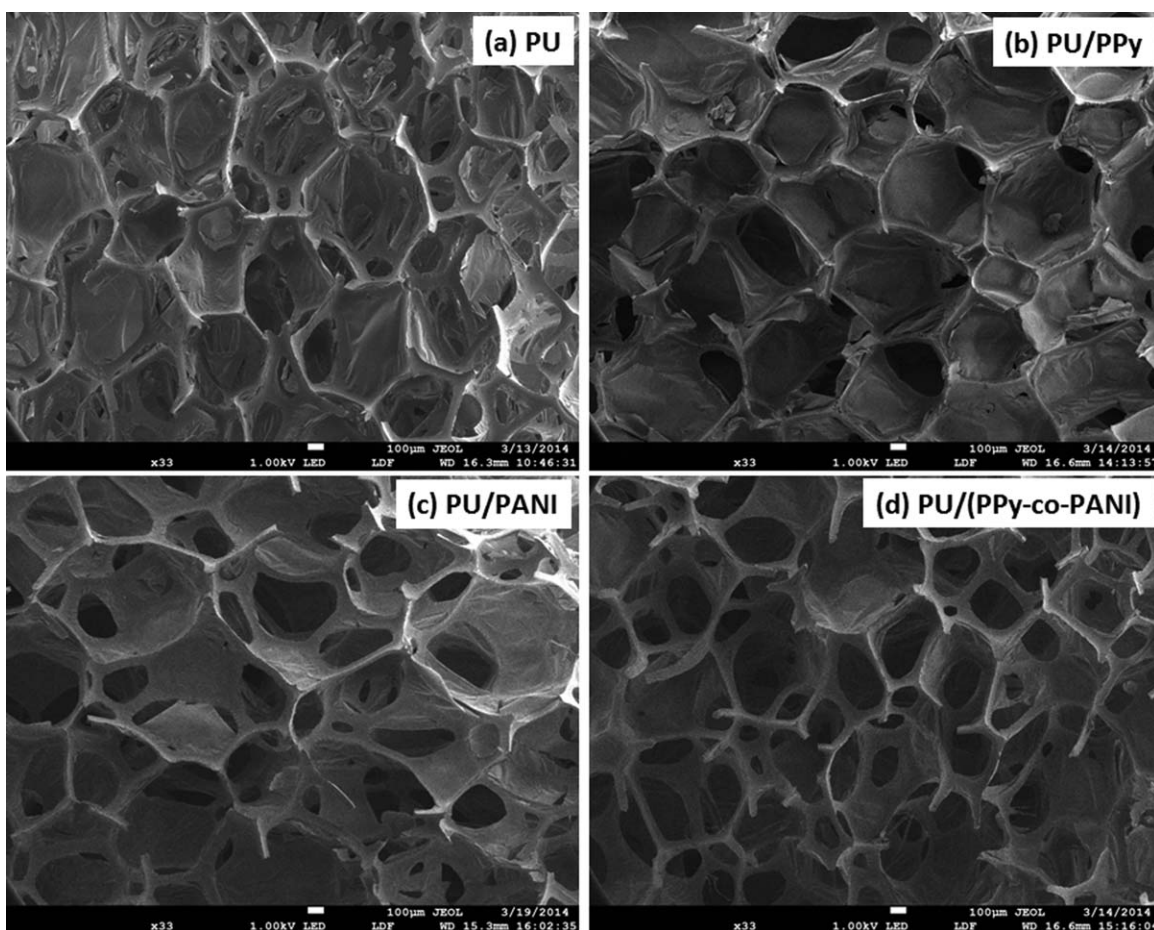

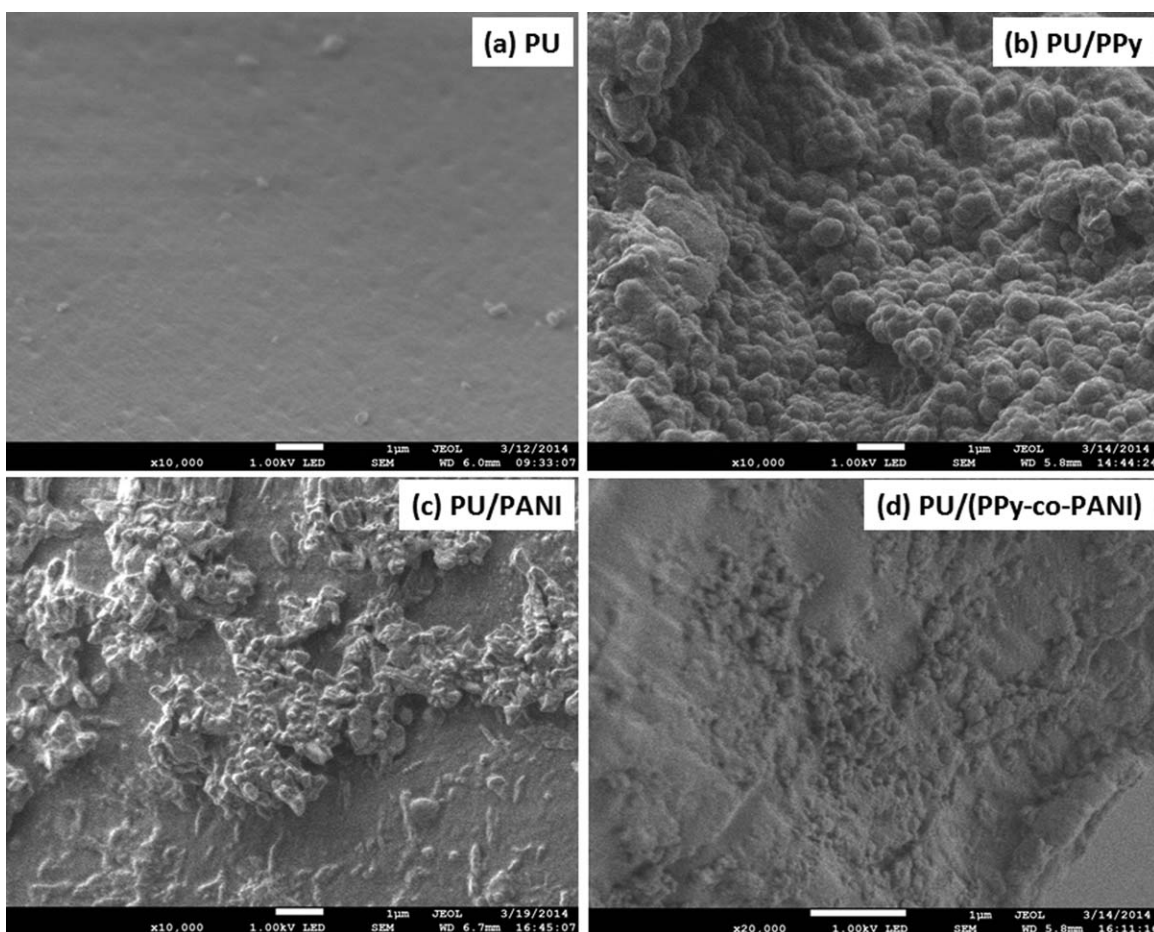**Figure 3.** SEM micrographs of PU foam and different supports synthesized (33 × magnifications).

Figure 4. SEM micrographs of PU foam and different supports synthesized. (a), (b), and (c) at 10,000× magnification while (d) at 20,000×.

However, when the copolymer of PPy and PANI was deposited onto the PU surface, very small spherical nanoparticles were formed with diameters between 80 and 150 nm. This is a result of PPy which tends to form spherical morphology and a complex interaction between the conducting polymers and the PU foam surface.

Due to the PPy and PANI morphology over the surface of the PU foam, increased surface area can be expected such that more microorganisms and organic molecules can have access to the modified surface. More importantly, the positively charged nature of PPy and PANI (Figure 2) increases adhesion of negatively charged bacteria to the surface through electrostatic attraction.[36,37]

The amounts of polymers attached to the PU foam determined by gravimetry for PU/PPy, PU/PANI, and PU/(PPy-co-PANI) were 9%, 8%, and 9%, respectively. The attachment of biomolecules or biologically active species to conductive nanostructures is a critical step to accomplish biofunctionality. The development of flexible designs that combines the structural features of nanostructured conductive polymers with the biofunctionality and biocompatibility required for the application is still considered the principal challenge in creating feasible bioactive systems.[38] Combining mechanical properties of PU with the biocompatibility from PPy and PANI, resulted in a material

that can be used for microorganism immobilization for applications like wastewater treatment.

Polyurethane is named after the urethane bond formed via the reaction of isocyanate with hydroxyl groups. Toluene diisocyanates (TDI) is one of the most used in flexible PU foam manufacturing (Figure 5). Figure 6 shows the FTIR spectra of the different materials synthesized and that of uncoated PU foam. The spectrum corresponding to the PU foam shows the characteristic signal of TDI, the peaks at 1715 cm^{-1} and 1636 cm^{-1} correspond to C=O stretching in urethane, the signal at 1600 cm^{-1} is due to C=C from the aromatic ring, the signal at 1228 cm^{-1} is ascribed to C—O, and the peak at 1080 cm^{-1} can be assigned to C—O—C[39] which demonstrates that a TDI was used in the PU synthesis. The most important signals of PANI can be seen in Figure 6 for PU/PANI and PU/(PPy-co-PANI) materials, which are: At 828 cm^{-1} due to C—H aromatic out-of-plane bending of 1,4-ring, at 1283 cm^{-1} from C—N stretching in QBcQ, QBB, and BBQ; at 1500 cm^{-1} ascribed to C=C stretching from B rings, and at 1578 cm^{-1} due to C=C stretching from Q rings.[38] On the other hand, the main signals of PPy in the spectrum of PU/PPy should be near to 1452 cm^{-1} (from C—C ring stretching), at 1547 cm^{-1} (from C=C backbone stretching), at 1312 cm^{-1} (C—H in-plane), and at 1178 cm^{-1} (from C—N stretching vibrations); however signals
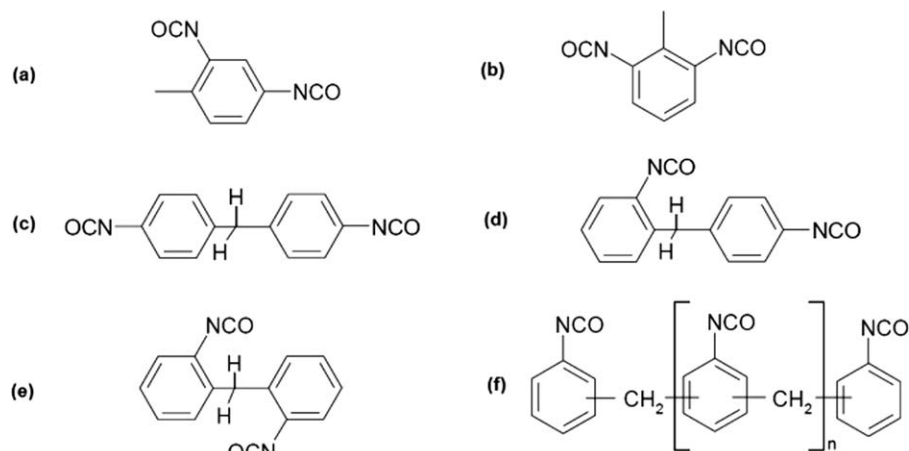
Figure 5. Toluene diisocyanates commonly used in PU foam manufacturing.

corresponding to PU overlapped with those corresponding to PPy. The FTIR spectrum of the PU/(PPy-co-PANI) contains some distinct features respect to PU/PPy and PU/PANI. For example, the broad band from 1620 to 1570 cm^{-1} observed only for copolymer of pyrrole and aniline onto PU foam should be due to the resonance of the quinoid phenyl ring C—C stretch of PANI at 1578 cm^{-1} and the C=C backbone stretching mode of PPy at 1547 cm^{-1}, which becomes a potent proof to demonstrate the direct linkage of aniline and pyrrole units.[40]

Thermogravimetric analysis was carried out to investigate the thermal properties of the PU/(PPy-co-PANI) composite, and the results are shown in Figure 7. As can be seen from this figure, the presence of conducting polymer attached to PU foam improves the thermal stability of composite. The initial thermal weight loss temperature of composite and pure PU was obtained as 274 and 283°C, respectively. The thermal decomposition temperature increased 9°C, suggesting that thermal stability of hybrid PU composite was improved considerably. The possible reason for this behavior is that conducting polymers can reduce the mobility of PU chains, inhibiting the PU chain reaction, and slowing the degradation process.[41] It can also be observed in Figure 7 that decompositions of both PU and PU/(PPy-co-PANI) composite show a second stage of weight

loss. In PU foam the second stage of decomposition is centered at 373°C, whereas for PU/(PPy-co-PANI) composite is displaced at 387°C. The first decomposition stage can be ascribed to the breaking of urethane bonds (isocyanate groups), and the later to ester decomposition from polyol segments.[42]

Performance of Supports in Batch Wastewater Treatment

Figure 8 shows the profile of COD removal as a function of time for the wastewater treatment using different supports of PU with conducting polymers synthesized in this work after microorganism immobilization. It can be seen that after 48 h of degradation, the COD decreases fast from 650 to 300 mg/L in all cases. This behavior can be explained in the following terms: The systems worked batchwise for a month for biofilm formation, this led to a kind of microorganism starvation inside the biofilm and when the "fresh wastewater" was added during the experiment; the biomass either stored this substrate instead of using it for direct growth, or absorbed and degraded it.[43] An increase in COD was observed for the PU/PPy material after 48 h, which might be due to desorption of some organic material from the support. However COD concentration starts to decrease, again, after 96 h of treatment. COD removal behavior for the PU foam and the PU/PANI support was very similar with a higher COD removal achieved using the PU/(PPy-co-
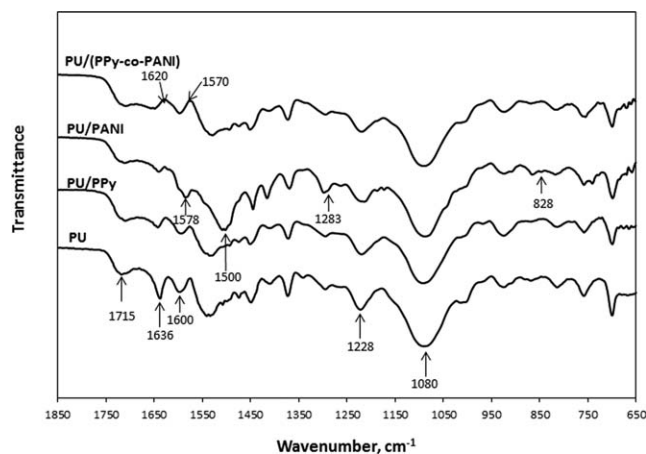

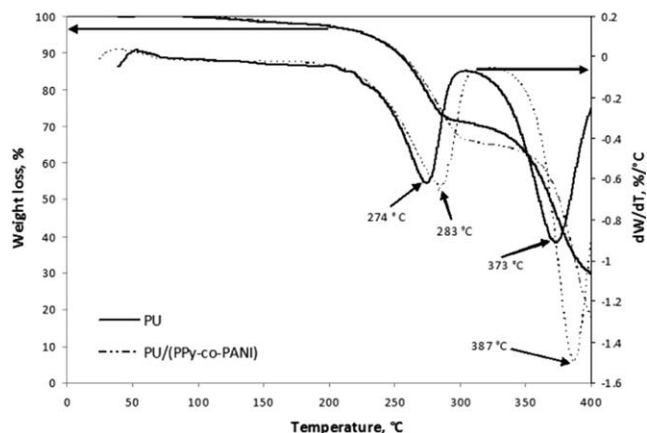**Figure 6.** FTIR spectra of different supports of PU with PPy and PANI.

Figure 7. Thermogravimetric analysis of PU foam and PU/(PPy-co-PANI) composite.
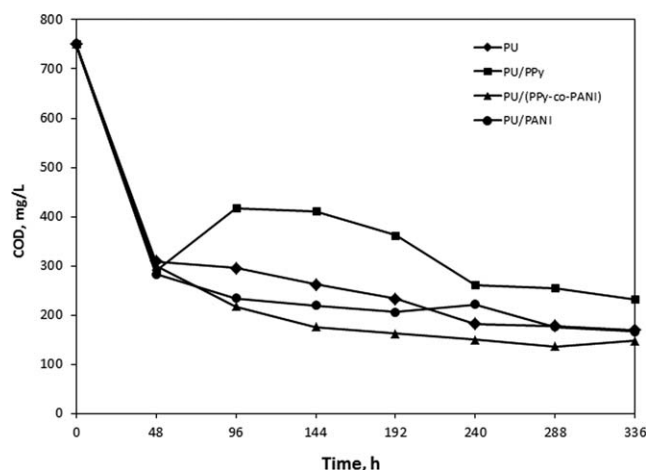
Figure 8. COD removal profiles using the synthesized PU foam supports.

Table II. Amount of Immobilized Biomass in PU and PU/(PPy-co-PANI) Supports in Anaerobic and Aerobic Conditions

Sample	g of biomass/g of support
PU, anaerobic	0.65
PU, aerobic	0.69
PU/(PPy-co-PANI), anaerobic	0.79
PU/(PPy-co-PANI), aerobic	0.84

80%; respectively in a period of 14 days. It can be also observed in Table I that the pH value remains practically constant around 8.0 except for the PU/PPy sample, which drops to a neutral value. Sulfates and nitrates concentration were measured at 0 mg/L by the end of treatment.

PANI) material. This implies that copolymers of PPy and PANI offer combined electrical properties promoting microorganism fixation. Also, the modified surface morphology strongly affected COD removal and, as it will be discussed later, the amount of immobilized microorganisms. In the case of PU/PPy occluded pores were observed, giving lower results in COD removal, even worse than the removal obtained with pure PU. Less occluded pores were observed for the PU/PANI material, however the support morphology was such that PANI formed irregular structures; thus superficial area was not increased to levels necessary to significantly enhance microorganisms immobilization. An optimized surface morphology was achieved for the PU/(PPy-co-PANI) support in which pores of the PU structures were not so occluded having globular morphology with enhanced superficial area for microorganisms immobilization.

Park et al.[44] used a carbonaceous material obtained by carbonization of dye sludge from a synthetic textile dyeing factory. This carbonaceous material was mixed with a Tween-85 surfactant solution and PU pre-polymer (Hypol-3000) to obtain a PU/carbonaceous composite to immobilize fungi (*Phanerochaetechrysosporium*) for COD removal of a dyeing wastewater. They observed from batch tests that COD using this material dropped from 500 to 350 mg/L after 24 h of treatment (30% of efficiency) and to 200 mg/L after 8 days (60% of efficiency). Table I shows the initial and final physicochemical characteristics of the wastewater used in the present work. As it is shown in Table I, the efficiency of COD removal for PU foam, PU/PPy, PU/PANI, and PU/(PPy-co-PANI) were 77%, 69%, 78%, and

Amount of Immobilized Biomass in Supports

The amount of biomass per gram of support was determined for PU/(PPy-co-PANI) and pure PU as previously described. The results are shown in Table II. It can be observed that the amount of immobilized biomass in the supports was higher in the aerobic than in the anaerobic conditions (6.15% higher for pure PU and 6.34% higher for PU/(PPy-co-PANI)). When comparing pure PU against PU/(PPy-co-PANI), immobilized biomass was 21.5% higher in PU/(PPy-co-PANI) under anaerobic conditions and 21.7% higher under aerobic conditions. These results are in accordance with those shown in Figure 8. Thus microorganism affinity towards the surface of the PU/(PPy-co-PANI) support was increased when compared with the naked PU surface under both anaerobic and aerobic conditions.

Figure 9 shows the SEM images of PU/(PPy-co-PANI) supports with immobilized biomass in anaerobic (a and b) and in aerobic (c and d) conditions. It can be visually inferred from Figure 9 that a higher biomass amount is present in aerobic than in anaerobic conditions. This agrees with the results shown in Table II. It can be observed that cell aggregates are formed in the matrix pores of the support and a thin biofilm attached to the inner surface of support. These immobilization patterns are similar to those described by Varesche et al.[45] whom observed polyurethane foam matrices taken from a fixed-film reactor treating glucose-based substrate. Gijzen et al.[46] reported on the adherence of methanogenic archaea to polyurethane foam matrices from a reactor treating organic acids as well. Morphologies resembling spirochaetes, bacillus and coccus can be observed. In

Table I. Physicochemical Characteristics of Wastewater Used in This Study Before and After COD Removal

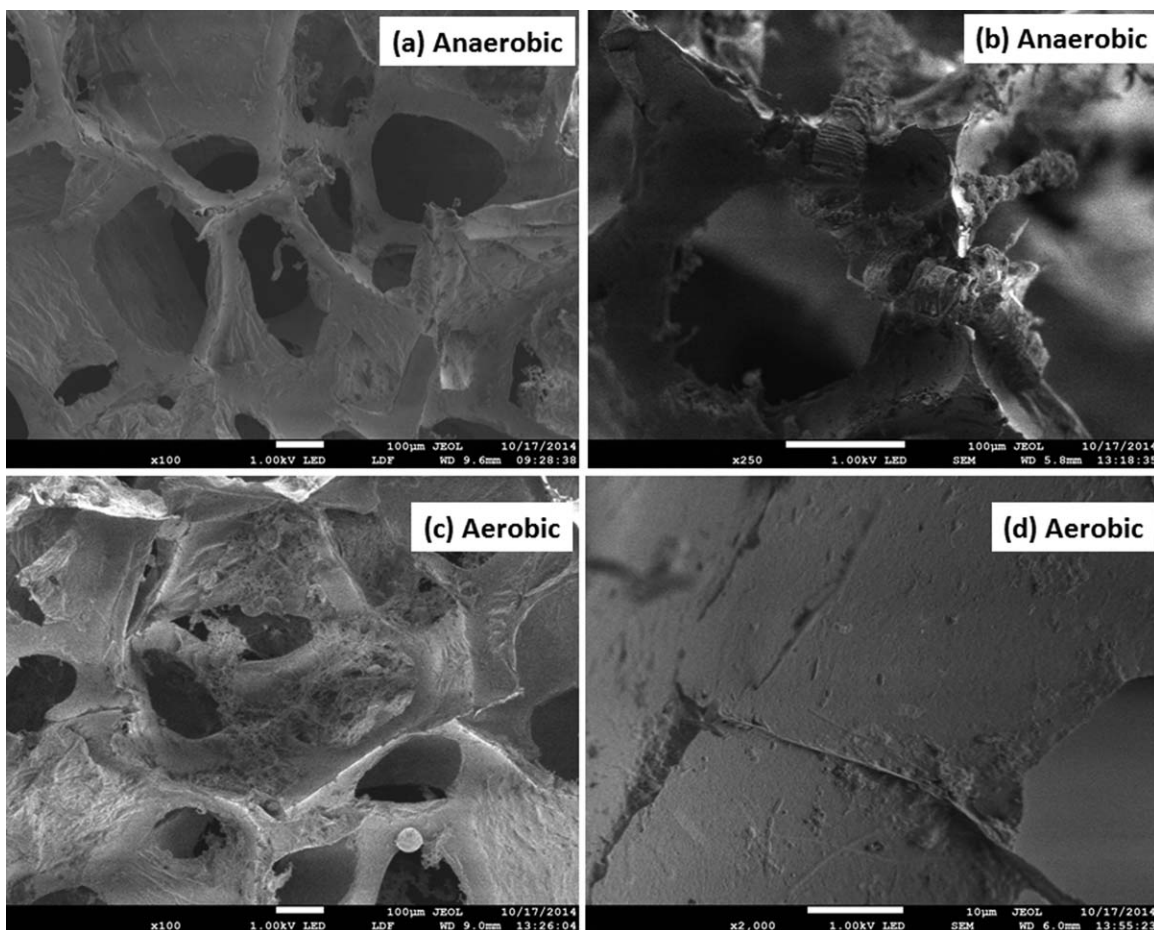| Sample	pH		Sulfates (mg/L)		Nitrates, (mg/L)		COD (mg/L)		COD removal efficiency
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	
PU	8.3	7.8	112	0	4	0	750	169.8	77%
PU/PPy	8.3	7.0	112	0	4	0	750	232.0	69%
PU/PANI	8.3	7.9	112	0	4	0	750	166.4	78%
PU/(PPy-co-PANI)	8.3	7.7	112	0	4	0	750	147.6	80%

Figure 9. Microbial colonization and attached biomass to PU/(PPy-co-PANI) support in anaerobic and aerobic conditions: (a) and (c) cell aggregates in the matrix pores, (b) and (d) thin biofilms attached to the surface of support.

anaerobic conditions a dark-green biomass was observed, whereas in aerobic conditions a white mucopolysaccharide attached to support was noticed. When wastewater treatment in PBR using only PU as support was run, a reddish color was observed in the anerobic reactor and in the aerobic reactor no color was observed. Thus the support of PU/(PPy-co-PANI) has selective microorganism immobilization. However additional work needs to be done to completely identify the cell colonization, this will be presented in a future work.

Performance of Supports in Continuous Flow in PBR Wastewater Process

Since a batch wastewater method requires a long time to achieve high efficiencies, a continuous flow is needed to accelerate the

COD removal process. According to the results observed batch-wise, the PU/(PPy-co-PANI) support was used to immobilize microorganisms in a sequential PBR wastewater treatment. Table III shows the results from the sequential PBR wastewater treatment at 24 h and 36 h of HRT under steady-state operation using four different influent COD concentrations (variations of COD of the influent were due to collection of municipal wastewater at different days). It can be observed that for 24 h of HRT, and using COD influent concentrations of 676 and 366 mg/L, the COD decreased to similar values in the anaerobic reactor (281 and 219 mg/L) with removal efficiencies of 58% and 40%, respectively; while the removal efficiencies for the aerobic reactor were 28% and 40%, respectively. Thus the overall COD removal efficiencies were 86% and 80%, respectively.

Table III. COD Concentrations of Influent and Effluents of Each Reactor and COD Removal Efficiencies (%)

Run/HRT	Influent (mg/L)	Anaerobic reactor (mg/L)	(%)	Aerobic reactor (mg/L)	(%)	Overall Efficiency (%)
Run A/24 h	676	281	58	93	28	86
Run B/24 h	366	219	40	73	40	80
Run C/24 h	289	99	66	72	9	75
Run D/36 h	642	90	86	38	8	94

According to these results the COD removal efficiency increased with the COD in the influent. This behavior has been previously reported by Montalvo et al.,[47] using zeolite as support, and by Ding et al.,[43] using gravel as support. On the other hand by increasing the HRT to 36 h, higher efficiency was obtained (94%). It can also be observed that COD removal is mainly verified in the anaerobic section of the PBR sequential system.

CONCLUSIONS

Electrically conducting supports of PU/PANI, PU/PPy, and PU/(PPy-co-PANI) were prepared and characterized. It was observed that conductivities for the supports were 7.3×10^{-9} S/cm, 7.4×10^{-10} S/cm, and 7.7×10^{-10} S/cm, respectively; when compared to plain PU foam. The combined mechanical properties of PU with the biocompatibility of PPy and PANI resulted in a material (PU/(PPy-co-PANI)) that was used for microorganism immobilization for municipal wastewater treatment, with COD removal efficiency of 80% in batch mode. This was ascribed to the well coating of PU structures and smaller globular morphologies with enhanced superficial area for microorganism immobilization. On the other hand, it was observed from the sequential PBR wastewater treatment that for 24 h of HRT and a COD influent concentration of 676 mg/L, an overall removal efficiency of 86% was achieved which raised to 94% when working with 36 h of HRT and a COD influent concentration of 642 mg/L.

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