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# Anionic Dye Removal with a Thin Cationic Polyaniline Coating on Cellulosic Biomaterial

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## ABSTRACT

This paper reports the development of novel adsorbent materials using polyaniline (PANI) grafted onto Posidonia (POS) fibers, aimed at efficiently removing phenol red (PSP), an anionic dye, from aqueous solutions. The synthesis involved the copolymerization of aniline grafted on the surface of POS and aniline monomer in solution, resulting in a chemically bound thin PANI layer on the POS bioadsorbent. Structural characteristics and binding affinities of these adsorbents with PANI under its emeraldine salt (POS@PANI-ES) or emeraldine base (POS@PANI-EB) forms are reported. The rapid adsorption kinetics observed is attributed to enhanced accessibility to PANI adsorption sites on the POS surface. The binding percentages of PSP to POS@PANI-ES and POS@PANI-EB materials were found to be 97% and 50%, respectively, after 15 minutes of contact time. The Langmuir model for localized adsorption sites and the Volmer model for non-localized adsorption as a mobile layer were fitted to the experimental adsorption isotherms of PSP to POS@PANI-EB and POS@PANI-ES, yielding the thermodynamic parameters of adsorption. The adsorption capacities of PSP on POS@PANI-EB and POS@PANI-ES were 37.8 and 71.5  $\mu\text{mol}\cdot\text{g}^{-1}$ , respectively. The adsorption of PSP remained above 80% at moderate salt concentrations around 0.1  $\text{mol}\cdot\text{L}^{-1}$ ; however, higher concentrations of NaCl and CaCl<sub>2</sub> in PSP solutions significantly reduced adsorption on POS@PANI-ES.

**Key words:** Posidonia, bio-adsorbent, polyaniline, adsorption, anionic dye.

## 1. INTRODUCTION

Industrial wastewater laden with residual dyes comes from different sources (e.g. dyeing or textile industries, pharmaceutical industries,...) and is considered a wide variety of organic pollutants, highly visible even at vanishing concentrations (1). Their direct release into the environment can lead to the accumulation of toxic substances resulting from the chemical or biochemical transformation of the dyes and the deterioration of the aquatic environment (2). Often, chemicals in industrial wastewater are difficult to biodegrade, and the inadequacy of treatments leads to their accumulation in the water cycle (3–5). Dye-laden industrial wastewater has been extensively studied by developing effective dye removal techniques to treat the dye effluents before discharging them into water bodies (6–10). Conventional physicochemical and biological methods of effluent treatment are expensive and sometimes unsuitable for large rivers due to their less cost-effective and difficult operational conditions. For the removal of organic dyes from aqueous media, many methods have been investigated. The most widely used techniques for water discoloration include adsorption, photodegradation, precipitation, coagulation and membrane filtration (11). The most powerful and practical discoloration treatment process among the available water treatment techniques is adsorption, in which recovery and recycling of adsorbent materials can be possible with cost-effectiveness and distinct advantages such as no release of toxic sludge. Nowadays, many inexpensive and commercially available adsorbents have been tried for water discoloration processes such as clays, zeolites, activated alumina, peat, biomasses, biopolymers, agricultural residues and industrial by-products (12). These adsorbents are able to adsorb many dyes contained in industrial aqueous effluents with high adsorption capacities, but the costs of regeneration are expensive because desorption of the dye molecules is not easy to achieve (13). In recent years, low-cost adsorbents including products of natural waste origin, such as fruit trees, egg shells, palm waste and date palm kernels have also been used (14). However, there is still a need to study new biomaterials with low-cost and high adsorption capacities. The objective of this study was to introduce modified *Posidonia* as an adsorbent for the removal of anionic dyes, such as phenol red considered a typical dye, from water by adsorption using depletion techniques.

*Posidonia oceanica* (POS), commonly known as Neptune grass or Mediterranean tapeweed, is an abundant biomass source suitable for producing high-value-added materials. Its ability as adsorbent to remove both organic and inorganic molecules has been shown (15–18). The main constituents of fibrous of POS materials consist of cellulose, lignin and hemicellulose. Its surface is rich in hydroxyl groups, which can be exploited for surface modification. It also contains other functional groups such as carboxylic acid and amide that can play an important role in the adsorption process. For example, carboxylic acid groups can contribute to the adsorption of positively charged species through ion

exchange or electrostatic interactions. At the same time, amide groups may be involved in hydrogen bonding or other interactions that affect the overall adsorption capacity and mechanism.

Phenol red or phenolsulfonphthalein (PSP), classified as an anionic dye, is a red crystal stable in air and highly soluble in water ( $0.77 \text{ g L}^{-1}$ ) (19). The molar mass ( $M_w$ ) of phenol red is  $354.38 \text{ g}\cdot\text{mol}^{-1}$ . It is a pH indicator that changes color from yellow below pH 6.8 to bright pink above pH 8.2. It is commonly used as an indicator in cell culture and various laboratory applications. It is widely used in various industrial processes and even in household products. One application that causes its release in the environment is the control of the pH and chlorination degree in swimming pools (20). The discharge of phenol red into wastewater raises significant environmental concerns related to its bioaccumulation by aquatic fauna. In addition, phenol red in wastewater can contribute to unpleasant odors and contaminate organic and inorganic substances, thereby exacerbating pollution and environmental problems in the long term. The toxicity of phenol red to micro-organisms and aquatic ecosystems highlights the importance of its effective removal from wastewater. Posidonia has a negative surface charge throughout the pH range; it requires surface modification by cationic polymer. Polyaniline polymer (PANI) was used in the present work because of its favorable chemical structure for electrostatic interactions with PSP. In addition, our previous work (21) have shown that the grafting process by copolymerization of aniline and surface-grafted aniline yields a very thin layer of grafted PANI with an average polymerization degree of approximately 4. A thin grafted layer is enough with regards to the application to adsorption because adsorption takes place on the surface. Using a low amount of grafted material is economically favorable.

To obtain a solid support with suitable functions for the covalent immobilization of the PANI polymer, the preparation involved grafting aniline groups onto the surface of Posidonia. These monomer reactive groups served as precursors for the development of a thin, rigid layer of polyaniline on the surface through their copolymerization with free aniline added in solution. Indeed, PANI in its emeraldine salt form (PANI-ES) is a cationic conjugated polymer produced by the conventional oxidative polycondensation of aniline monomer in an acidic medium. Undoubtedly, the delocalization of charges on the polymer backbone makes PANI a hydrophobic polymer despite its overall polycationic nature. This cationic and hydrophobic structure of PANI-ES allows hydrophobic interactions assisted by electrostatic interactions with aromatic and anionic PSP molecules. Indeed, in addition to electrostatic interactions, conjugated aniline moieties create favorable  $\pi$ - $\pi$  stacking interactions with polyaromatic molecules, as for example organic dyes (21). PANI-ES is prepared by oxidative polymerization of aniline in a concentrated aqueous medium of hydrochloric acid (1 M HCl). PANI-ES requires doping the conjugated polymer by protonation of nitrogen atoms with an acid. Several examples of adsorbent materials prepared from PANI doped under its acidic form have been reported. A more sophisticated preparation of PANI grafted onto the surface of mesoporous

silica revealed a selective adsorption capacity for organic sunscreens (22). As simpler is better, the present work dealt with the polymerization of aniline aiming at the formation of a thin layer of PANI coating the POS bio-adsorbent by copolymerization with the surface-grafted aniline (POS@ANI). POS@PANI-EB was prepared by dedoping POS@PANI-ES in a basic medium. The produced materials were evaluated and compared by means of adsorption tests involving kinetics of the adsorption process and adsorption equilibrium isotherms. This study presents a novel adsorbent material with promising applications in the removal of anionic dyes from wastewater. By exploiting the unique properties of PANI-coated POS, this research contributes to the development of sustainable and cost-effective solutions for wastewater treatment.

## **2. Materials and methods**

### **2.1. Reagents and chemicals**

Aniline (ANI), N-[3-(trimethoxysilyl)propyl]aniline (APTMS), diisopropylethylamine (DIEA), ammonium persulfate and phenol red also known as phenolsulfonphthalein (PSP) were supplied by Sigma-Aldrich. All solvents used were of analytical grade and all solutions were made with Milli-Q water of 18 M $\Omega$  cm resistivity.

### **2.2. Characterization methods**

IR spectra were recorded with a Bruker IFS 55 Equinox FTIR spectrometer in ATR mode. <sup>13</sup>C CP-MAS NMR spectra of native and modified Posidonia materials were performed on a Bruker Avance III 500 ultra-shield PLUS spectrometer. All prepared Posidonia materials were subjected to thermogravimetric analyses (TGA) carried out on a TG209F1 Netzsch instrument under a dynamic atmosphere of nitrogen. Zeta potentials were measured by electrophoresis with a Malvern Zetasizer Nano ZS instrument, with 0.05 wt% aqueous suspensions at different pH values. The  $\zeta$  potential was calculated from the electrophoretic mobility under the Smoluchowski approximation. The measurements were carried out using the suspensions of materials in ultra-pure water and adjusting the pH of each (values between 2 and 10) by the addition of 0.1 M NaOH or HCl solution. The suspensions were kept under constant agitation at ambient temperature for 24 h to determine the final equilibrium pH. PSP absorbance was measured using an ultraviolet-visible (UV-vis) spectrophotometer Varian Cary 50 type. The XRD profiles were obtained using a PANalytical X'Pert PRO Multi-Purpose diffractometer with Cu K $\alpha$  radiation at a generator voltage of 45 kV and current of 40 mA. The full nitrogen adsorption-desorption isotherms were performed at 77 K using a Micromeritics ASAP2020 instrument. Before nitrogen adsorption measurements, the MIPs were heated at 150 °C under vacuum. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area of MIPs. The porous volumes were calculated from the experimental desorption branch according to the Barret–Joyner–Halenda (BJH) method. Measurements of nitrogen

adsorption-desorption isotherms were performed at 77 K using a Micromeritics ASAP2020 instrument. Before nitrogen adsorption measurements, the samples were degassed at 150 °C under vacuum. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Optical microscopy pictures of aqueous suspensions were taken between plate and cover slip using a Leica DMLM microscope. Scanning electron microscopy (SEM) pictures were taken at the Centre Technologique des Microstructures facility of the University of Lyon 1 (CTmu, <https://microscopies.univ-lyon1.fr/>) using a FEI Quanta 250 FEG microscope working under 5 kV acceleration and secondary electron detection. Powder samples were spread on aluminum stubs covered with a double sided conductive adhesive carbon disks (Agar, Oxford Instruments) and metallized by sputtering Cu in a Leica MED 020 coating system.

### **2.3. Preparation of Posidonia biomaterials**

Posidonia balls were collected from Cheba-Mahdia beach on the east coast of Tunisia. The fibers of biomass balls have been manually disentangled, extensively washed with large volumes of deionized water to remove sand and salt commonly present in seawater, and then dried in the open air. The obtained Posidonia fibers were washed in a Soxhlet extractor with ethanol for 24 h and dried in an oven at 50 °C for 48 h until the mass of the fibers became constant. The dry biomasses were crushed, then sieved in order to recover particles of homogeneous size (50 µm) washed repeatedly with distilled water, and oven dried for 24 h at 50–60 °C. The Posidonia samples were stored in a desiccator for later use.

### **2.4. Grafting of aniline monomer to Posidonia surface**

The anhydrous process involving a direct reaction of surface silanols was investigated for the grafting of N-[3-(trimethoxysilyl)propyl]aniline silane (APTMS) as a dense monolayer at the surface of Posidonia; 500 mg of dried Posidonia (POS) was dispersed by magnetic stirring in 17 mL of anhydrous toluene containing 400 mg of APTMS and 400 mg of DIEA. The suspension was heated at reflux under a nitrogen atmosphere for 12 h. The modified Posidonia (POS@ANI) was rinsed with 30 mL of THF, dried at 60 °C overnight, and stored under vacuum for subsequent uses.

### **2.5. Coating modified Posidonia with polyaniline**

The aniline monomer grafted to the surface of prepared POS@ANI was copolymerized with aniline; 500 mg of POS@ANI was dispersed in 100 mL of HCl aqueous solution at pH = 3 in the presence of 186 mg (2 mmol) of aniline monomer. The reaction mixture was cooled in an ice bath and 5 mL of a solution of ammonium persulfate in water was added dropwise to the solution. The reaction was allowed to proceed at 0–5 °C for 8 h. The POS@PANI-ES powder was isolated by filtration and washed repeatedly with water until the absence of the characteristic UV absorption of PANI oligomers at 400 and 800 nm in the filtrate. Then, the solid powder was dried under a vacuum at 60 °C for 24 h.

The POS@PANI-EB was prepared by treatment of POS@PANI-ES with 0.3 M NH<sub>4</sub>OH solution for 24 h. The list of abbreviations of materials used to carry out this work is reported in [Table 1](#).

**Table 1.** List of the studied materials with their abbreviations.

Materials	Abbreviations
Posidonia powder (medium size 50 μm)	POS
Posidonia modified with aniline	POS@ANI
Posidonia modified with PANI-EB	POS@PANI-EB
Posidonia modified with PANI-ES	POS@PANI-ES

## 2.6. Binding experiments

### 2.6.1. Standard solutions

Stock standard solutions (300 μmol L<sup>-1</sup>) of phenol red were prepared in water. Working solutions ranging from 10 to 250 μmol L<sup>-1</sup> were obtained by successive dilutions in water at neutral pH. Both stock standard and working standard solutions were stored in a refrigerator at 5 °C until their use.

### 2.6.2. Effect of adsorbent mass

The experiments were carried out by agitating 5 mL of 50 μmol·L<sup>-1</sup> PSP solutions with varying amounts of unmodified or modified Posidonia (POS, POS@PANI-ES, and POS@PANI-EB) at 298 K. Subsequent to centrifugation of each sample, the residual PSP concentration was measured using a UV–vis spectrophotometer at the appropriate wavelength ( $\lambda_{\max} = 430$  nm). The adsorbed percentage (%A, %) was calculated using the following equation:

$$\%A = (C_0 - C_e) \frac{100}{C_0} \quad (1)$$

where  $C_e$  (mol L<sup>-1</sup>) is the equilibrium concentration of PSP solution,  $C_0$  is the initial PSP concentration (mol L<sup>-1</sup>),  $V$  (L) is the volume of PSP solution and  $m$  (g) is the mass of the adsorbent.

### 2.6.3 Kinetic study

Kinetic studies were established to evaluate the effect of contact time on PSP adsorption and to determine the equilibrium time. The adsorption process was conducted for the time interval of 2, 5, 8, 12, 16, 20, 25, 30, 40 and 50 min at 298 K. The initial concentration of PSP aqueous solution was fixed at 50 and 100 μmol·L<sup>-1</sup>. 18 mg of each prepared material was mixed with 5 mL of PSP solution and the mixture was then magnetically stirred at 380 rpm for different contact times. After each stirring time, the mixture was centrifuged at 5000 rpm. The supernatant was analyzed by UV–vis absorbance analysis at  $\lambda_{\max} = 430$  nm. The percentage of adsorbed amount at time  $t$  ( $Q_t$ , mol·g<sup>-1</sup>) was calculated using the following equation:

$$Q_t = \frac{V}{m} [C_0 - C_t] \quad (2)$$



where  $C_t$  ( $\text{mg}\cdot\text{L}^{-1}$ ) is the residual PSP concentration at time  $t$ ,  $C_0$  is the initial PSP concentration ( $\text{mg}\cdot\text{L}^{-1}$ ),  $V$  (L) is the volume of PSP solution and  $m$  (g) is the mass of the material.

#### 2.6.4. Adsorption isotherms

All adsorption measurements were performed by the depletion method in water since real environmental samples were essentially aqueous media. For equilibrium adsorption, the material (18 mg) was immersed in 5 mL of water containing PSP with various concentrations ranging from 10 to 175  $\mu\text{mol}\cdot\text{L}^{-1}$  and kept in a thermostatic water bath shaker and shaken at 380 rpm constant shaking rate at a constant temperature. The mixture was stirred for 60 min equilibration time, then centrifuged at 5000 rpm. The residual PSP concentration ( $C_e$ ,  $\text{mol}\cdot\text{L}^{-1}$ ) in the supernatant was determined by UV-vis absorbance analysis ( $\lambda_{\text{max}} = 430$  nm) using the calibration curve. The dynamic adsorption capacity ( $Q_e$ ,  $\text{mol}\cdot\text{g}^{-1}$ ) of PSP was calculated according to the following equation.

$$Q_e = \frac{V}{m} (C_0 - C_e) \quad (3)$$

where  $C_0$  ( $\text{mol}\cdot\text{L}^{-1}$ ) and  $C_e$  ( $\text{mol}\cdot\text{L}^{-1}$ ) are the initial and equilibrium concentrations of the PSP solution,  $V$  (L) is the volume of the PSP solution,  $m$  (g) is the mass of the solid material.

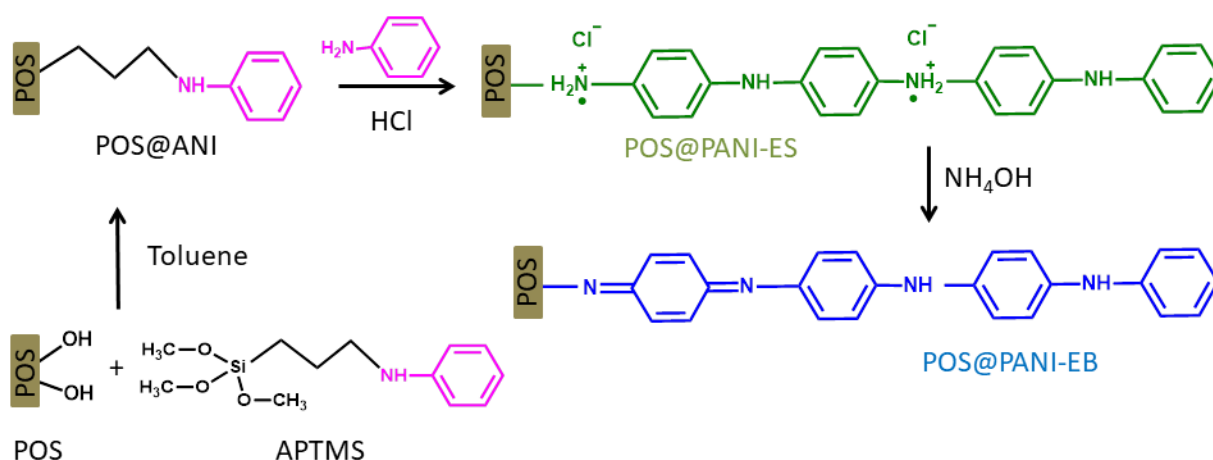
### 3. Results and discussion

#### 3.1. Synthesis and characterization of polyaniline grafted on Posidonia

The Posidonia biomaterial exhibits numerous surface functional groups that serve as readily accessible sites for grafting. These functional groups present on the surface of Posidonia, such as hydroxyl, carboxyl, and amino groups, offer versatile and reactive points for chemical interactions and modifications. This inherent reactivity allows for the seamless incorporation of various functional moieties, including polyaniline in this case, through well-established chemical methods. Indeed, the preparation of POS@PANI-ES and POS@PANI-EB was achieved in two synthetic steps (Figure 1): N-[3-(trimethoxysilyl)propyl]aniline (APTMS) containing aniline group was firstly grafted onto POS surface to provide POS@ANI with anchored aniline monomers available for subsequent copolymerization. The silane coupling agent was covalently attached to the POS surface by a direct condensation reaction of surface functional groups of Posidonia with the methoxy groups of APTMS involving an anhydrous process. Such a process allows binding a dense monolayer of aniline monomer at the surface of Posidonia. Thus, the aniline groups in APTMS immobilized onto POS biomaterial have strong reactivity and can effectively be involved in the oxidative polymerization of aniline. The POS@PANI-ES material was prepared by oxidative copolymerization of aniline groups of POS@ANI and aniline monomer added in the acidic reaction medium. The polymerization of aniline was achieved in an acidic medium (HCl concentration in the range  $10^{-3}$  M, pH = 3) for producing the cationic PANI-ES form grafted on the surface of Posidonia. At this pH, aniline is



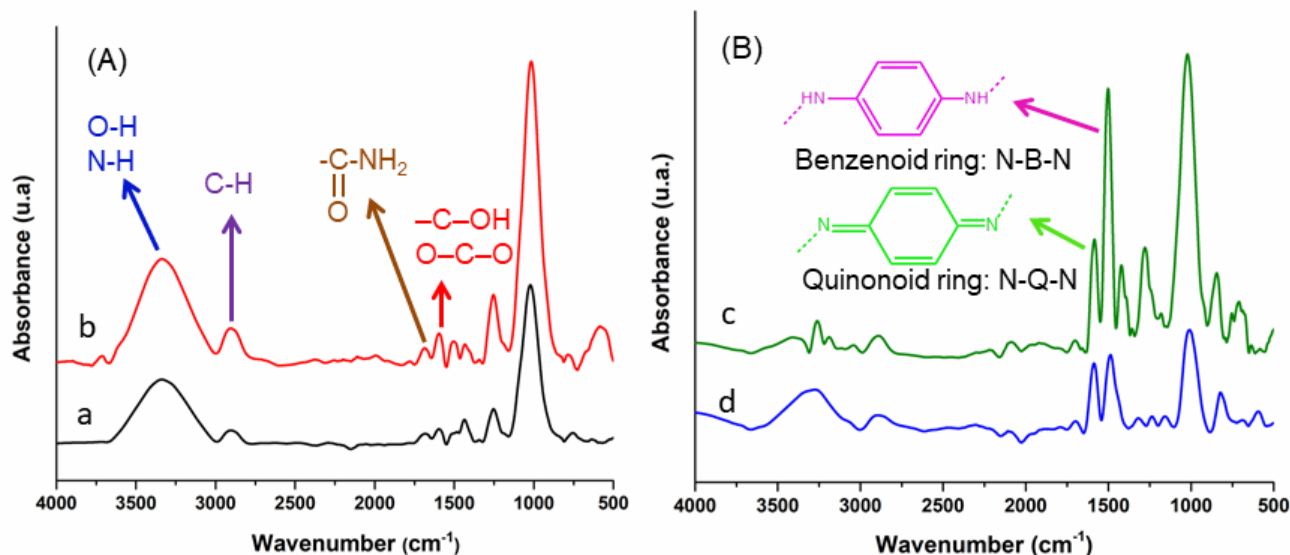
predominantly protonated under anilinium form and the generated polyaniline is under its emeraldine salt form. A grafted PANI-ES layer was formed at the surface of Posidonia. POS@PANI-EB was prepared by a treatment of POS@PANI-ES with 0.3 M aqueous ammonia solution.



**Figure 1.** The PANI synthesis route in emeraldine salt and emeraldine base forms immobilized on POS biomaterial.

Infrared spectra of POS, POS@ANI, POS@PANI-ES and POS@PANI-EB were collected in the wavenumber range 500–4000  $\text{cm}^{-1}$  (Figure 2A and 2B). The characteristic bands of the POS biomaterial indicate the presence of carbonyl, hydroxyl, and methoxy functional groups, which are characteristics of cellulose, hemicellulose, and lignin, respectively (Figure 2A). The presence of -OH and -NH vibrations was demonstrated by the broad band in the range 3700–3000  $\text{cm}^{-1}$ . The asymmetric and symmetric C–H stretching vibrations located at 2971 and 2886  $\text{cm}^{-1}$  are assigned to the alkyl groups, respectively. The band at 1617  $\text{cm}^{-1}$  was attributed to the amide -C(O)NH<sub>2</sub> bond, while the one at 1425  $\text{cm}^{-1}$  was related to the deformation vibration of -C–OH, featuring contributions from the symmetrical stretching vibration O–C–O of the carboxylate group. In particular, this band at 1425  $\text{cm}^{-1}$  is also known as the crystal band. The band shows the crystal order of cellulose (23). The IR spectrum of POS@ANI presented in Figure 2A shows both characteristic bands of Posidonia and bands corresponding to the grafts: symmetric and asymmetric stretching vibrations of C–H bonds at 2908 and 3330  $\text{cm}^{-1}$  and C=C stretching of aniline aromatic ring at 1688 and 1596  $\text{cm}^{-1}$  (22). The characteristic bands of APTMS appeared at the same wavelength as those of the POS biomaterial. However, an increase in the intensity of these bands was observed for POS@ANI, confirming the grafting of the silane carrying the aniline monomer. IR spectra of POS@PANI-ES and POS@PANI-EB (Figure 2B) clearly indicated the successful polymerization of aniline in the presence of the POS biomaterial. The spectra showed absorption bands at 1589  $\text{cm}^{-1}$  and 1486  $\text{cm}^{-1}$ , associated with C=C stretching vibrations of the quinonoid and benzenoid rings of PANI, respectively. These two peaks confirmed the formation of the emeraldine form of PANI. The corresponding bands of the emeraldine base form were slightly shifted. This red shift can be explained

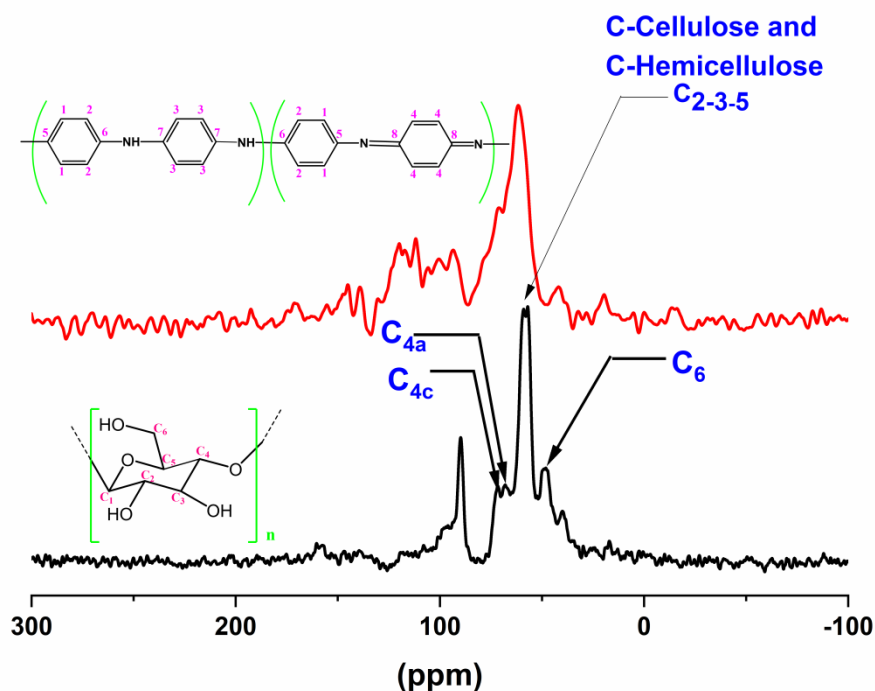
by the formation of hydrogen bonds between the hydroxy groups on the surface of the POS and the  $-NH-$  group of the emeraldine base. The decrease in the vibrational intensity of the benzenoid band in the POS@PANI-EB spectra is attributed to the transformation of the polaron lattice into a quinonoid structure within the polymer chain during the deprotonation process (24).



**Figure 2.** IR spectra of (A): POS (a), POS@ANI (b), (B): POS@PANI-ES (c) and POS@PANI-EB (d).

<sup>13</sup>C CP MAS NMR spectroscopy is the most effective method for the characterization of the lignocellulosic and polymeric materials and is able to provide detailed information directly on the solid sample. A typical example of <sup>13</sup>C NMR spectra of POS and POS@PANI-EB are shown in Figure 3. The solid-state <sup>13</sup>C NMR spectrum of the POS exhibits strong signals of carbons in the range of 20–190 ppm, which mainly correspond to the different carbons of cellulose, hemicellulose and lignin components of Posidonia fibers. The strong signals in the region between 50 and 107 ppm are attributed mainly to the different carbons of cellulose and hemicelluloses (25). Nevertheless, NMR technique is able to differentiate the crystalline versus the paracrystalline domains since the carbons located within the interior crystalline regions have a distinct chemical shift from the carbons located on the crystal surfaces or paracrystalline domains. Cellulose consists of crystalline and non-crystalline phases in different ratios, depending on its natural source. The only signal that can be mainly assigned to lignin is at 56 ppm belonging to the methoxy group of the aromatic moieties. In addition, the region between 106 and 180 ppm is specific for the aromatic carbons of lignin. The <sup>13</sup>C CP-MAS NMR analysis of POS@PANI-ES (Figure 3) showed, in addition to the characteristic peaks of POS, a broad peak (110–160 ppm) composed of several resonances characteristic of reduced polyaniline form (26). In particular, the peak at 153 ppm corresponds to the carbon atom in the

quinoid ring, which cannot rotate around the bent bond of the imine group (=N–) in the idealized repeating unit of PANI. The peaks at 155 and 157 ppm indicate the polycondensation of the aniline, which confirms the immobilization of the PANI layer on the surface of POS biomaterial. The characteristic peaks of POS shifted in the POS@PANI-EB spectra because of the interaction between functional surface of POS and PAN-EB chains.



**Figure 3.**  $^{13}\text{C}$  MAS NMR spectra of POS (black spectrum) and POS@PANI-EB (red spectrum).

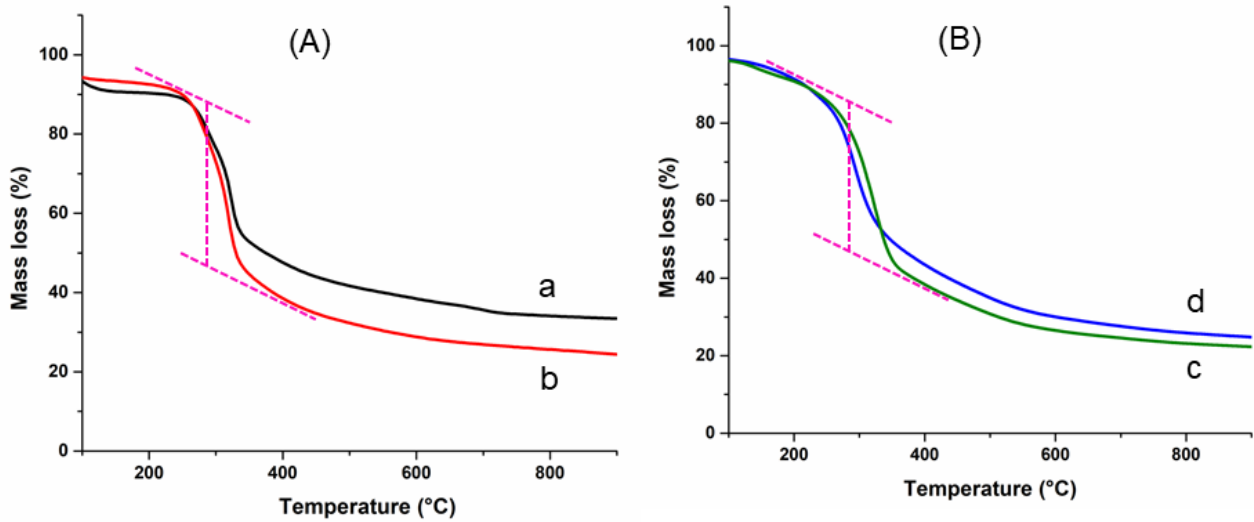
Thermogravimetric analysis was used to estimate the surface density of POS@ANI, POS@PANI-EB and POS@PANI-ES materials (Figure 4). The TGA patterns of POS@ANI showed a slight mass loss from 100 to 200 °C, corresponding to the evaporation of moisture. The main mass loss occurred between 250 and 600 °C, attributed to the thermal decomposition of the organic phase composed of hemicellulose (the most thermally unstable compound), cellulose from the POS biomaterial and the silane grafts (Figure 4A). The TGA of POS@PANI-EB and POS@PANI-ES (Figure 4B) show a single broad step, corresponding to the thermal decomposition of the entire organic content of POS and the polyaniline surface-grafted materials. The mass loss attributed to PANI was determined as the difference between the two mass losses of POS@PANI and POS@ANI. The thermal decomposition of POS@PANI-EB and POS@PANI-ES extended up to 900 °C. The mass loss due to the grafted organic layer was estimated considering that thermal cleavage occurred at the functional surface bond, the molar mass of the lost moiety of APTMS,  $-(\text{CH}_2)_3\text{-NH-C}_6\text{H}_5$ , was  $M_{mol}(\text{APTMS}) = 134 \text{ g}\cdot\text{mol}^{-1}$ , and the surface density ( $SD$ ) was calculated as:

$$SD \text{ (mol}\cdot\text{g}^{-1}\text{)} = \frac{\frac{m(\text{POS@ANI})}{100-m(\text{POS@ANI})} - \frac{m(\text{POS})}{100}}{M_{mol}(\text{APTMS})} \quad (4)$$

The surface density of PANI was calculated from the mass loss of POS@PANI-EB and POS@PANI-ES, which corresponded to a mean aniline polymerization degree of 4. The determination of the surface density of POS@PANI is written as:

$$SD = \frac{M(\text{POS@PANI}) - M(\text{Pos@ANI})}{100 \times M_{mol}(\text{grafted PANI})} \quad (5)$$

where  $M(\text{POS@PANI})$  is the mass loss of POS@PANI,  $M(\text{POS@ANI})$  is the mass loss of POS@ANI, and  $M_{mol}(\text{grafted PANI})$  is the molar mass of the average repeat units of grafted aniline.



**Figure 4.** TGA thermograms of (A): POS (a) and POS@ANI (b); (B): POS@PANI-ES (c) and POS@PANI-EB (d).

Elemental analyses confirmed the presence of the organic silane group and polyaniline polymers in the POS@ANI and POS@PANI materials. The surface density of aniline was calculated by determining the mass percent of carbon and nitrogen in the grafted POS materials:

$$SD \text{ (mol}\cdot\text{g}^{-1}\text{)} = \frac{\% C}{100 \times nC \times 12} \quad (6)$$

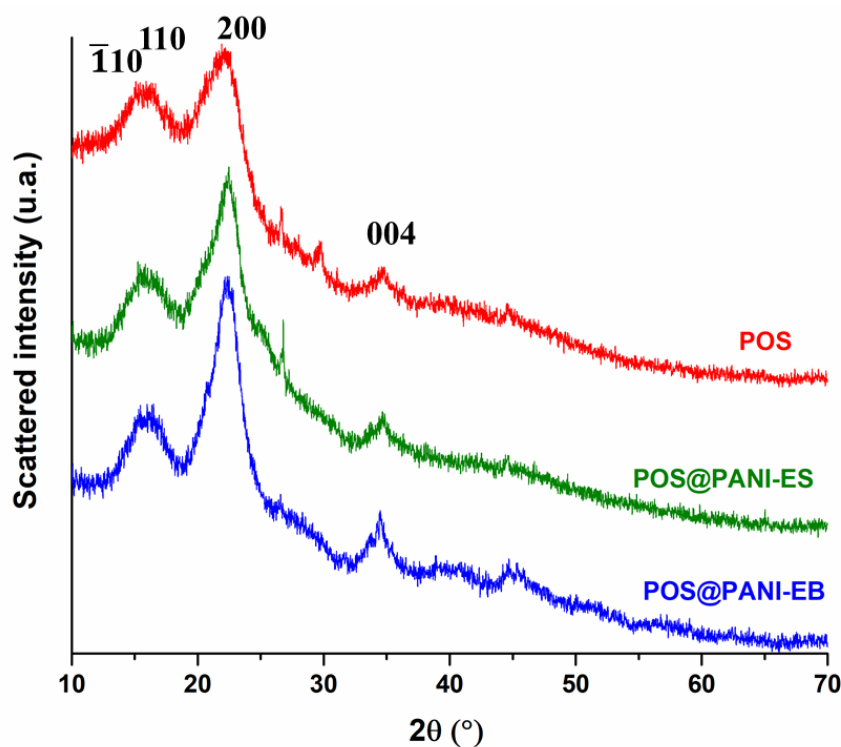
$$SD \text{ (mol}\cdot\text{g}^{-1}\text{)} = \frac{\% N}{100 \times nN \times 14} \quad (7)$$

The surface density of aniline in the POS@ANI grafts (Table 2) is close to the theoretical density of a densely packed monolayer of aniline molecules (estimated to be between 2000 and 5000  $\mu\text{mol}\cdot\text{g}^{-1}$ ) (27,28). This dismissed the possible formation of a thick polysiloxane layer by polycondensation of the organosilane. The surface density of PANI for POS@PANI-EB and POS@PANI-ES calculated from TGA and elemental analysis is shown in Table 2.

**Table 2.** Surface density of grafts for POS@ANI, POS@PANI-EB and POS@PANI-ES determined from TGA and elemental analysis.

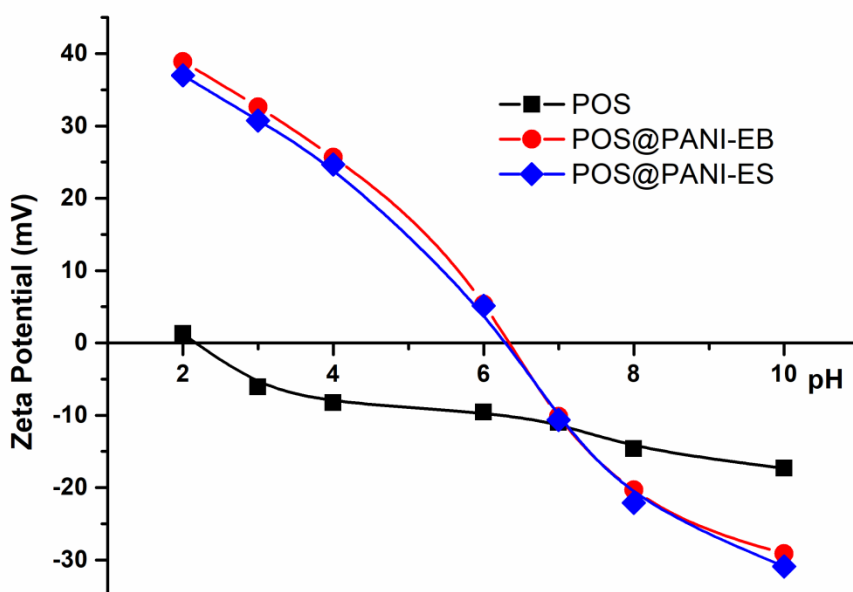
Materials	EA				TGA	
	% C	% N	$SD$ (C) (mmol·g <sup>-1</sup> )	$SD$ (N) (mmol·g <sup>-1</sup> )	Mass loss (%)	$SD$ (mmol·g <sup>-1</sup> )
POS	39.75	0.91	-	-	49.09	-
POS@ANI	47.60	8.26	6.50	5.25	55.08	5.91
POS@PANI-ES	50.48	8.65	0.72	0.69	74.07	0.64
POS@PANI-EB	49.92	8.56	0.58	0.53	75.08	0.54

The crystalline structures of POS, POS@PANI-ES and POS@PANI-EB materials were investigated by using XRD analysis (Figure 5). All samples exhibited four characteristic peaks detected at 15.22°, 16.31°, 22.24° and 34.70°, assigned to planes  $\bar{1}10$ , 110, 200 and 004 of the monoclinic lattice of type I cellulose (29). The peak observed in the POS pattern at  $2\theta = 29^\circ$  is attributed to mineral impurities that are largely presented in sea biomass (23). A supplementary peak was observed in the POS@PANI-ES pattern at 25.33° (110 plane, interplanar distance of 5 Å) corresponding to PANI in its emeraldine form (30). Moreover, the absence of the peak at  $2\theta = 29^\circ$  indicated the total removal of mineral impurities after the acidic treatment in the polymerization medium. Finally, the diffraction peaks of POS@PANI-ES and POS@PANI-EB were slightly narrower and sharper than for the pristine POS, indicating an increase in crystallinity after the prolonged immersion on the acidic polymerization medium.



**Figure 5.** XRD patterns of POS, POS@PANI-EB and POS@PANI-ES.

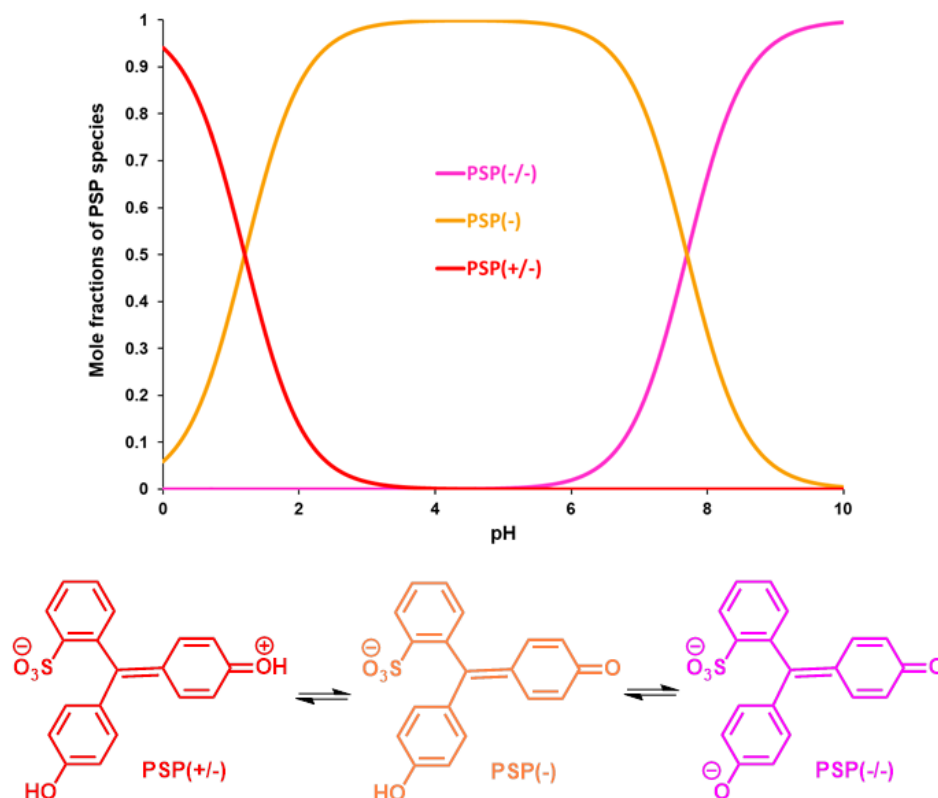
The pH is a crucial parameter in the adsorption process because it strongly influences the charges of the molecules in the solution and the surface charge of the adsorbent. The  $\zeta$  potential of POS, POS@PANI-EB and POS@PANI-ES was measured as a function of pH, providing the isoelectric point or point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of the materials (Figure 6). The determination of the  $\text{pH}_{\text{PZC}}$  is essential for understanding the adsorption process, especially when electrostatic forces are involved, as is the case with the PANI polymer. The isoelectric point of POS@PANI-ES was determined to be  $\text{pH}_{\text{PZC}} = 6.4$ , which is significantly different from the isoelectric point of the unmodified POS biomaterial ( $\text{pH}_{\text{PZC}} = 2$ ). This  $\text{pH}_{\text{PZC}}$  value is consistent with that of the pure emeraldine salt form of PANI (31), confirming that the outer surface of the material is indeed composed of PANI under its emeraldine salt form coating the entire surface of the POS biomaterial. These results indicate that the surface charge of POS coated with PANI is positive for  $\text{pH} < 6.4$  and negative for  $\text{pH} > 6.4$ . Moreover, it is worth noticing that POS@PANI-EB and POS@PANI-ES have the same surface charge at a given pH because POS@PANI-EB converts to POS@PANI-ES in an acidic environment through proton doping, and conversely, POS@PANI-ES transforms into POS@PANI-EB in a basic environment through dedoping. The  $\zeta$  potential data of POS@PANI-EB and POS@PANI-ES of Figure 6 are superimposed for this reason. Therefore, all the present adsorption experiments were performed by dispersing the POS@PANI-EB and POS@PANI-ES in pure water for their ionic form is kept.



**Figure 6.** Zeta potential of POS, POS@PANI-ES and POS@PANI-EB as a function of pH.

PSP adsorption to Posidonia coated with PANI and other sorbents is expected to be considerably influenced by its ionization state. Indeed, the PSP is a complex organic compound having several ionizable functional groups. Phenol red has two  $\text{pK}_a$  and hence can exist as three ionic forms, cationic, zwitterionic or anionic, under acidic, neutral and alkaline conditions, respectively, as show in

**Figure 7.** At low pH, this dye is zwitterionic with the ketone group being protonated and a negative charge on the sulfate group. Over the pH range 6.8 to 8.2, the ketone group is deprotonated, resulting in an overall negative charge of PSP. Aqueous speciation of PSP was also considered following the reactions below that show all its possible solution species:

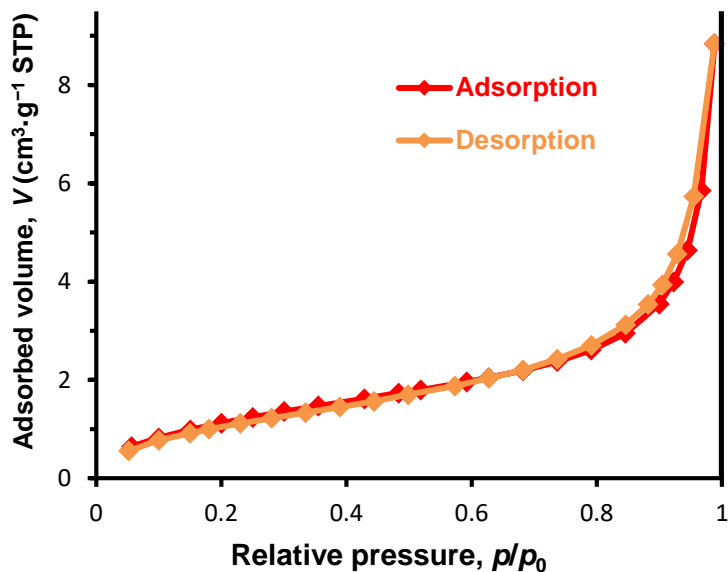


**Figure 7.** Structure and pH-dependent speciation of PSP. The graph is plotted using the  $\log(K_a)$  values of PSP, where PSP(+/-), PSP(-), and PSP(-/-) represent the different species of PSP.

The specific surface area was measured by nitrogen adsorption experiments at 77 K according to the BET method (Figure 8). The adsorption and desorption branches were superimposed, showing that there is negligible mesoporosity. There is no significant microporosity detected in a  $t$ -plot. The specific surface area determined from the BET equation in the relative pressure range  $p/p_0 = 0.05$ – $0.30$  was  $1.1 \text{ m}^2 \cdot \text{g}^{-1}$  for POS,  $4.7 \text{ m}^2 \cdot \text{g}^{-1}$  for POS@ANI and  $4.0 \text{ m}^2 \cdot \text{g}^{-1}$  for POS@PANI-ES. The specific surface area of pristine POS was quite low. Grafting the organosilane increased the specific surface area probably because of the roughness of the grafted layer. Finally, copolymerization of

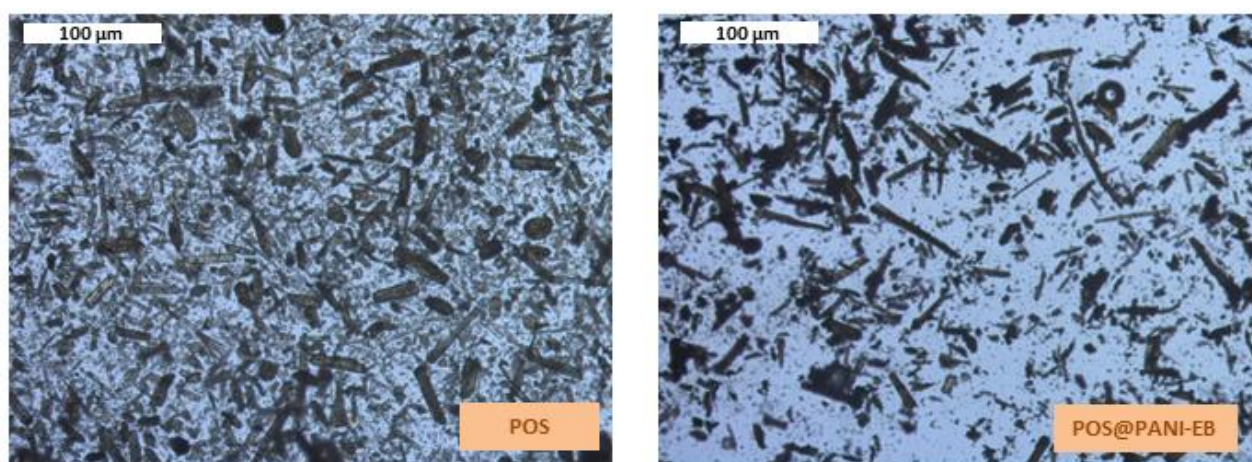


aniline giving POS@PANI-ES kept the specific surface area, as its measured decrease was small and rather insignificant.



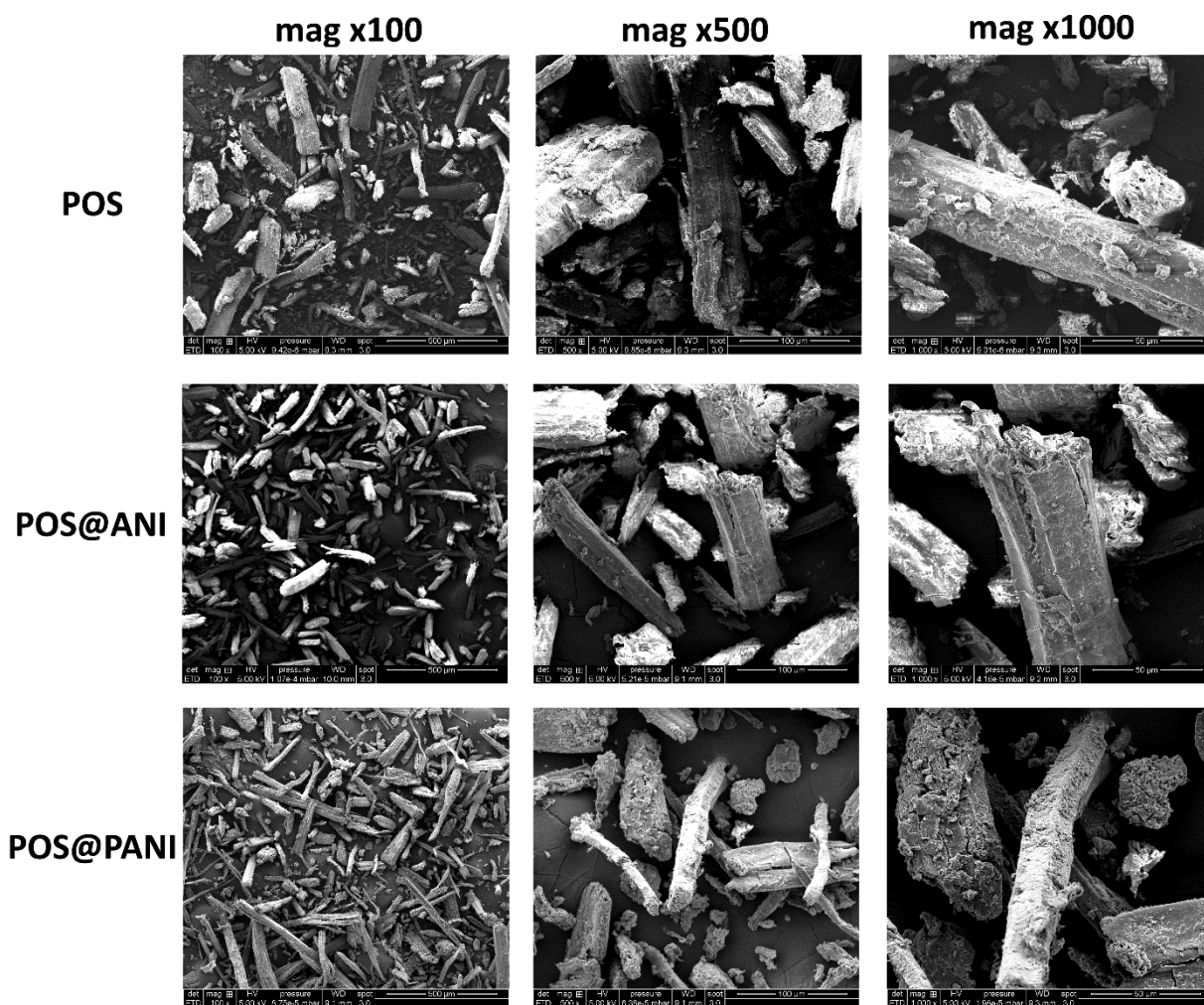
**Figure 8.** BET nitrogen adsorption and desorption isotherms of POS@ANI.

The morphology of POS and POS@PANI-EB was studied by optical microscopy. Different dispersions of POS and POS@PANI-EB in water were observed (Figure 9). POS material showed individual fibers with regular shape, clear and smooth surface. The approximate fiber length is 30–50  $\mu\text{m}$  with a width of 17  $\mu\text{m}$ . After the three chemical modification steps, the size of POS@PANI-EB remained constant, demonstrating the stability of the morphology of the material throughout the modification process.



**Figure 9.** Optical microscopy pictures of POS, and POS@PANI-EB in water.

Scanning electron microscopy (SEM) provided higher resolution pictures that supplemented the optical microscopy. SEM pictures of POS, POS@ANI and POS@PANI powders (Figure 10) revealed the same pieces of fibers as optical microscopy. Pictures at higher magnification showed the surface morphology being essentially smooth with some crazes and a few protruding lumps of amorphous material. Grafting aniline and growing polyaniline strands at the surface did not change the morphology. Indeed, the grafting process yields a thin PANI layer. Possible adhesion of PANI particles (coming from homopolymerization of aniline in aqueous solution) on POS fibers have not been observed.



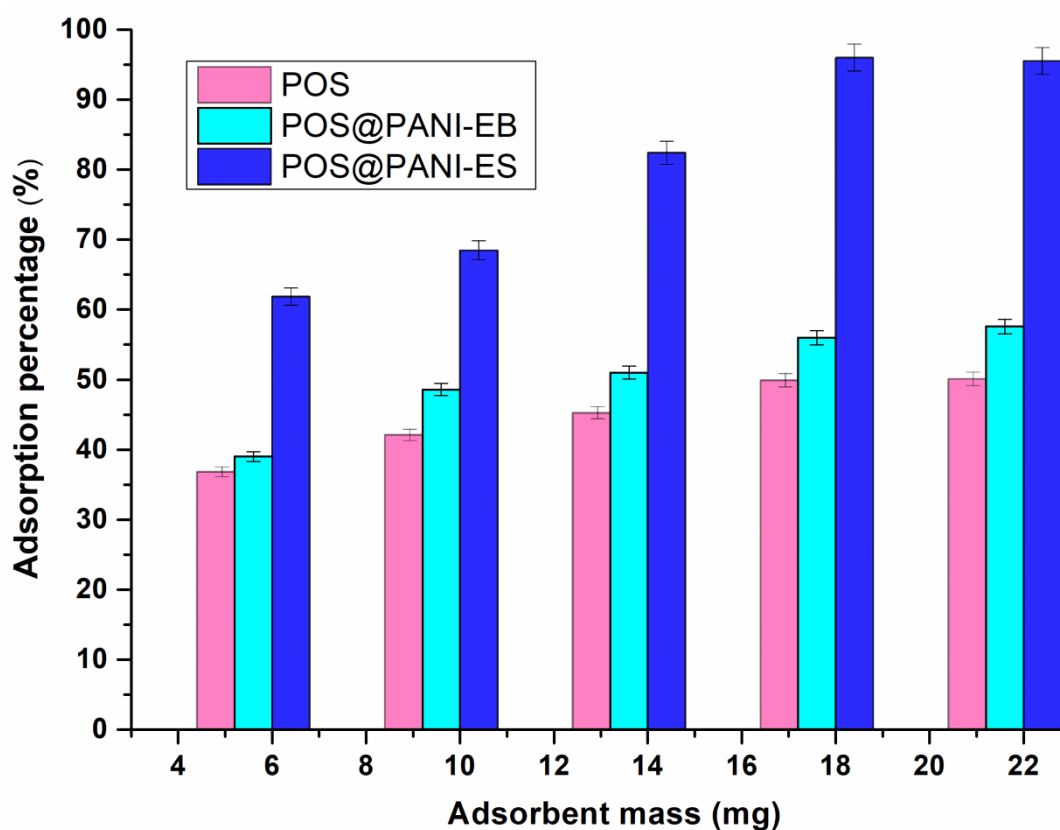
**Figure 10.** SEM pictures of POS, POS@ANI and POS@PANI powders at the three magnifications  $\times 100$ ,  $\times 500$  and  $\times 1000$ .

### 3.2. Performance for adsorption of Phenol Red

#### 3.2.1. Influence of adsorbent quantity

Different amounts of adsorbent from 6 to 22 mg dispersed in 5 mL aqueous medium were investigated. From the histogram shown in Figure 11, it can be seen that when using a mass of 18 mg

of POS@PANI-ES, the maximum capacity for the uptake of the PSP dye reaches approximately 96%. This performance is significantly superior to that of the other POS materials used, which show uptake capacities in the range of 45% to 55%. To maintain a congruent number of available adsorption sites, it is essential to match the fixed amount of PSP to the adsorbent distribution in the solution. Above a certain mass threshold, there is a slight decrease in the adsorption rate. This decrease may indicate the presence of a supplementary interaction between PSP molecules and native or modified *Posidonia* bioadsorbents. A competitive interplay between material particles containing PSP fractions and free adsorbents may be responsible for this phenomenon. Therefore, it is advisable to use an adsorbent mass of  $\leq 18$  mg. This avoids ineffective overdosing. An adsorbent mass of 18 mg has been selected for future studies focusing on the determination of adsorption capacity by saturation of all accessible sites.

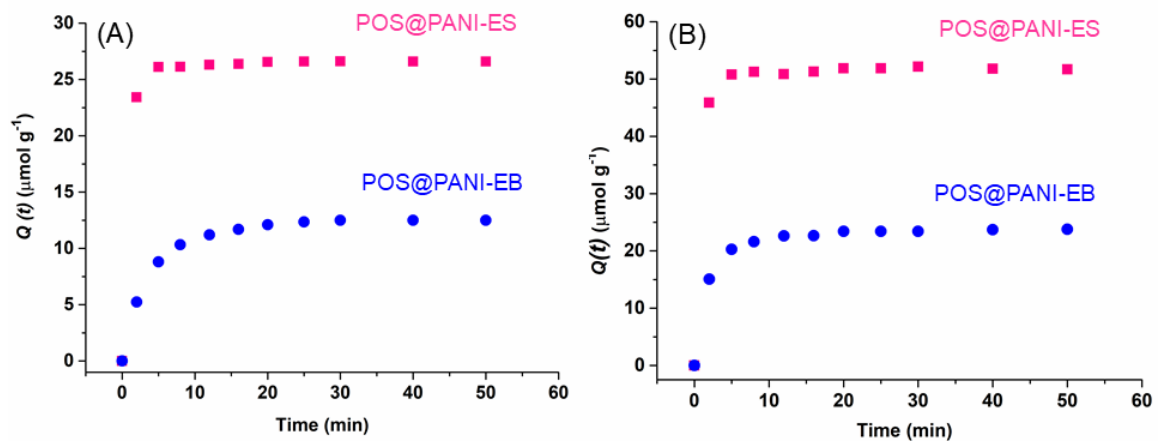


**Figure 11.** Mass effect of native and modified *Posidonia* materials on adsorption of PSP aqueous solution. Solution volume = 5 mL; concentration =  $50 \mu\text{mol}\cdot\text{L}^{-1}$ ; contact time = 60 min; and temperature = 298 °K.

### 3.2.1. Adsorption kinetics

Adsorption kinetics is a critical parameter for evaluating the effectiveness of an adsorbent. The objective was to compare the adsorption performance between PANI-EB and PANI-ES grafted onto the surface of *Posidonia*, considering their distinct characteristics, particularly different surface

charges. This focused comparison offers valuable insights into the adsorption behavior of these materials, enhancing our understanding of their potential applications in wastewater treatment. The impact of contact time on PSP adsorption onto POS@PANI-EB and POS@PANI-ES at concentration of PSP ( $5 \cdot 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  and  $10^{-4} \text{ mol}\cdot\text{L}^{-1}$ ) was measured in adsorption kinetics experiments using the depletion method (Figure 12). At the tested PSP concentrations, the adsorption uptake of PSP onto POS@PANI-ES material was significantly higher compared to the POS@PANI-EB material during the adsorption equilibration period. Indeed, the binding to POS@PANI-ES material was remarkably fast, increasing from 85% in 2 min to 97% in 15 min, while POS@PANI-EB enhanced from 25% in 2 min to 50% after 15 min of contact time. Such variation on mass transfer rate can be attributed to the nature of the interaction involved: the adsorption on POS@PANI-ES relies on an electrostatic interaction, whereas in the case of POS@PANI-EB, it is influenced by hydrogen bond formation. A typical time scale taken from the scarce experimental data is indeed much shorter than the typical time spanning from minutes to hours (32).



**Figure 12.** Adsorption kinetics experiments onto POS@PANI-EB and POS@PANI-ES from PSP solution at concentrations of (A):  $50 \mu\text{mol}\cdot\text{L}^{-1}$  and (B):  $100 \mu\text{mol}\cdot\text{L}^{-1}$  at 298 K.

Kinetic models were applied to evaluate the experimental results for POS@PANI-ES and POS@PANI-EB. Commonly used models for assessing the adsorption mechanism include the pseudo-first-order (33) and pseudo-second-order (34) models (Figure 13).

The pseudo-first order model, established by Lagergren, describes the adsorption kinetics where the rate is first-order with respect to the surface concentration of available adsorption sites (35). The adsorption rate at time  $t$  is proportional to the difference between the amount adsorbed at equilibrium  $Q(\infty)$  and the amount adsorbed at time  $t$ ,  $Q(t)$ :

$$\frac{dQ(t)}{dt} = k_1[Q(\infty) - Q(t)] \quad (9)$$

Integration using  $Q(0) = 0$  gives:



$$\ln[Q(\infty) - Q(t)] = \ln[Q(\infty)] - k_1 t \quad (10)$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the kinetic constant of pseudo-first order, and  $Q(\infty)$  and  $Q(t)$  are the adsorbed amounts at equilibrium and a given time  $t$ .

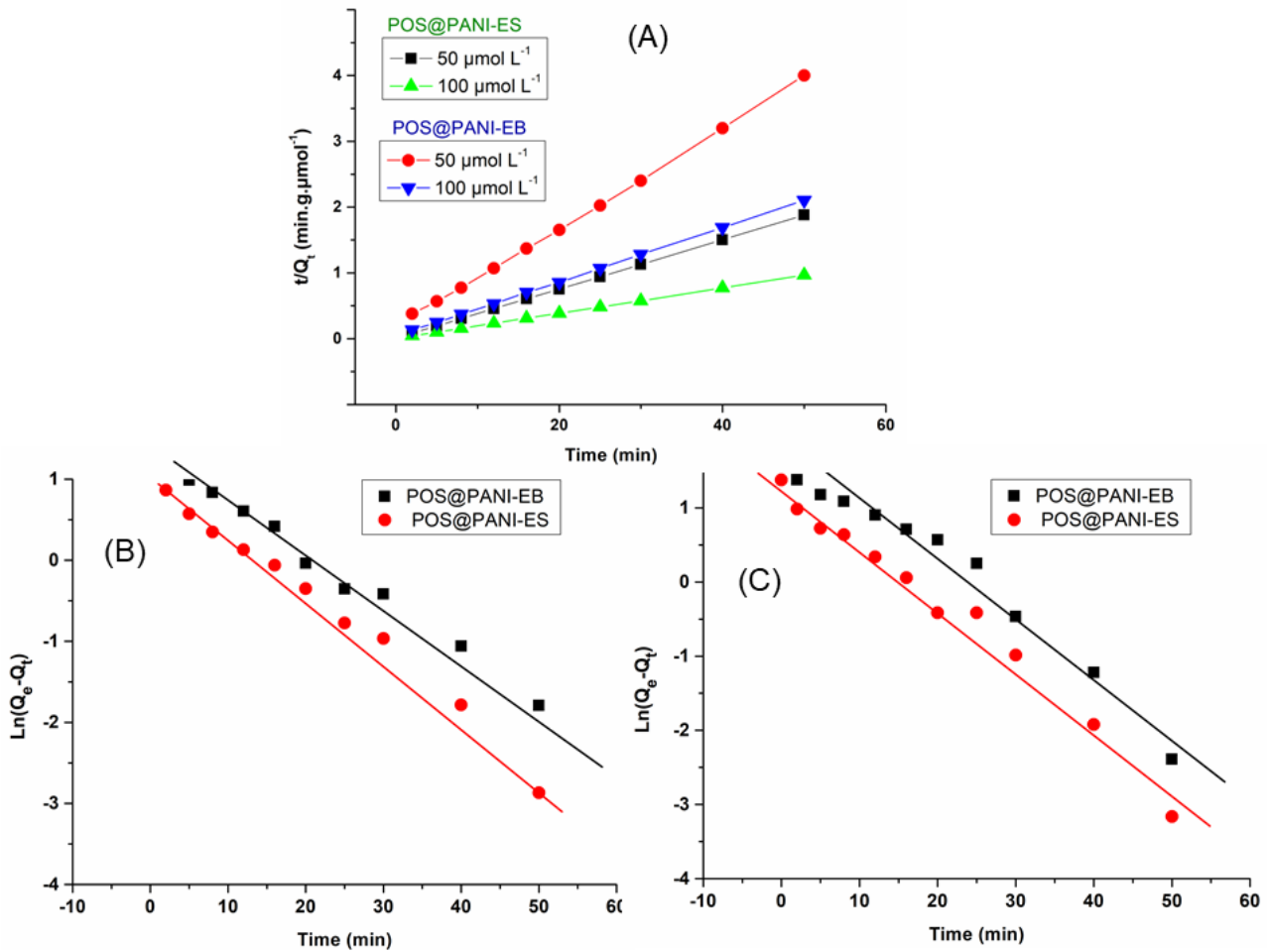
The non-linear form of the pseudo-second-order adsorption rate equation, as introduced by Blanchard (36), is frequently employed to describe the binding kinetics of ions to solid supports (34). This equation can be expressed as follows:

$$\frac{dQ(t)}{dt} = k_2[Q(\infty) - Q(t)]^2 \quad (11)$$

Integration of Eq. 11 using  $Q(0) = 0$  yields

$$\frac{t}{Q(t)} = \frac{1}{k_2 Q(\infty)^2} + \frac{1}{Q(\infty)} \quad (12)$$

where  $k_2$  ( $\text{g} \cdot \mu\text{mol}^{-1} \cdot \text{min}^{-1}$ ) is the kinetic constant of pseudo-second order and  $Q(\infty)$  and  $Q(t)$  are the adsorbed amounts at equilibrium and a given time  $t$ .



**Figure 13.** (A) Pseudo-second order kinetics model for adsorption of PSP onto POS@PANI-ES and POS@PANI-EB at concentrations 50  $\mu\text{mol} \cdot \text{L}^{-1}$  and 100  $\mu\text{mol} \cdot \text{L}^{-1}$ . Pseudo-first order kinetics model for adsorption of PSP onto POS@PANI-ES and POS@PANI-EB at concentration (B) 50  $\mu\text{mol} \cdot \text{L}^{-1}$  and (C) 100  $\mu\text{mol} \cdot \text{L}^{-1}$ .

According to the data in Table 3, the rate constants for the pseudo-first-order and pseudo-second-order models of POS@PANI-ES were lower than those found for POS@PANI-EB. Nevertheless, from the pseudo-second-order model, it is evident that the adsorption on POS@PANI-ES occurs approximately 3 to 5 times faster than on POS@PANI-EB, further supporting the application of the adsorption process using biomaterials for wastewater decontamination, which indeed requires rapid adsorption to allow a short operating time of the process and high efficiencies to remove organic pollutants. The fast kinetic processes observed in the case of POS@PANI-EB result from the presence of its positive charge, which enhances its attraction to the negatively charged molecules, promoting interactions through electrostatic forces. In contrast, the absence of a positive charge in POS@PANI-ES decreases its attraction to negatively charged particles, relying more on weaker hydrogen bonding interactions. In addition, the values of adsorption uptake at equilibrium calculated from the pseudo-second order model and the pseudo-first order model are closer to the experimental values. Thus, the pseudo-second-order model was considered as better than the pseudo-first-order kinetic model because it closer fitted to the experimental data ( $R^2 > 0.99$ ). Similar kinetic behavior was also observed for the adsorption of dyes on polyaniline-coated filter paper (37).

**Table 3.** Kinetic parameters of the pseudo-first order and pseudo-second order models of the adsorption study of PSP onto POS@PANI-ES and POS@PANI-EB materials.

Materials	$C_0$ ( $\mu\text{mol L}^{-1}$ )	$Q_{e,exp}$ ( $\mu\text{mol g}^{-1}$ )	Pseudo-first-order model			Pseudo-second-order model		
			$k_1$	$Q_{e,calc}$ ( $\mu\text{mol g}^{-1}$ )	$R^2$	$k_2$	$Q_{e,calc}$ ( $\mu\text{mol g}^{-1}$ )	$R^2$
POS@PANI-ES	50	26.6	0.061	25.3	0.991	0.010	24.3	0.999
	100	51.6	0.055	55.9	0.966	0.012	52.1	0.999
POS@PANI-EB	50	12.5	0.084	11.1	0.989	0.032	13.2	0.999
	100	23.8	0.083	25.3	0.981	0.040	24.3	0.999

### 3.2.2. Adsorption isotherms

The adsorption isotherm is a well-established tool for describing the interactive relationship between adsorbent and adsorbate over a range of concentrations. Experimental isotherm data are also used to describe adsorbent surface affinity and properties. Equilibrium adsorption isotherms were measured for the adsorption of PSP on POS@PANI-EB and POS@PANI-ES after an equilibration time of 60 min. Their analysis using thermodynamic models has been done with the Langmuir and Volmer theoretical models. The Langmuir isotherm is a classical model that considers homogeneous and independent binding sites on the surface of the adsorbent. Maximum adsorption is achieved when all

sites are occupied, resulting in a plateau in the adsorption isotherm. The underlying assumptions of the Langmuir model are satisfied for the localized adsorption of PSP on adsorption sites. The Langmuir adsorption isotherm for adsorption site on adsorbent assumes its classical form as follows (38):

$$Q_e = Q_{max} \frac{K C_e}{1 + K C_e} \quad (14)$$

where  $Q_e$  ( $\text{mol}\cdot\text{g}^{-1}$ ) is the adsorbed density in equilibrium with a solution of concentration  $C_e$  ( $\text{mol}\cdot\text{L}^{-1}$ ) is described by two parameters, the maximum adsorption capacity  $Q_{max}$  corresponding to density of adsorption sites, and the adsorption equilibrium constant  $K$  considered as a quasi-chemical equilibrated reaction of adsorbing molecules and surface sites.

The Volmer model is based on the same assumptions as those given by the Langmuir model regarding the energy homogeneity of the adsorbent surface and the absence of interactions between the adsorbed molecules. This model describes adsorption on a surface for non-localized (mobile) adsorption isotherm. The adsorbed molecules can diffuse freely on the surface, which makes the difference with the Langmuir model. The Volmer equation is written according to the following expression (39):

$$C_e = \frac{1}{K} \frac{\theta}{1-\theta} e^{\frac{\theta}{1-\theta}} \quad (15)$$

where  $\theta$  is the surface coverage,  $\theta = Q_e/Q_{max}$ , and  $K$  is the binding constant for adsorption equilibrium.

The Volmer isotherm differs from the Langmuir one by the supplementary term  $e^{\frac{\theta}{1-\theta}}$ . This relationship in the form of  $C_e$  as a function of  $Q_e$  was inverted into  $Q_e$  as a function of  $C_e$  by numerical resolution of equation (21).

The Langmuir and the Volmer adsorption isotherms were fitted to the experimental data by minimizing the average relative error function (*ARE*, equation 13) by non-linear regression.

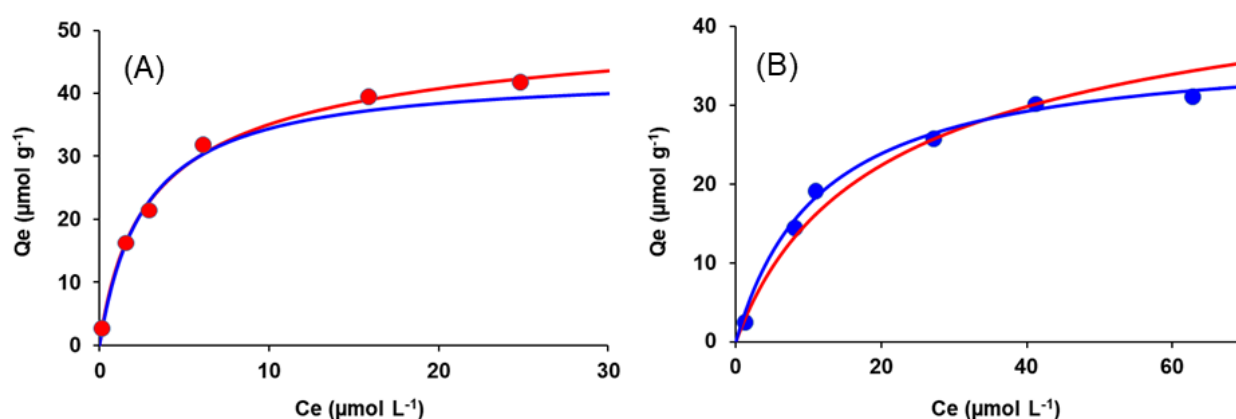
$$ARE = \frac{1}{n-p} \sum_{i=1}^n \left| \frac{Q_{exp} - Q_{calc}}{Q_{exp}} \right| \quad (13)$$

where  $n$  and  $p$  are the number of data points and fitted parameters respectively,  $Q_{exp}$  and  $Q_{calc}$  are the experimental and fitted adsorption capacities at equilibrium respectively.

As an important feature, modeling experimental adsorption data allows the discrimination of the mechanisms of adsorption and the related physicochemical interactions. The models of Volmer and Langmuir were fitted to the experimental adsorption isotherms of POS@PANI-ES and POS@PANI-EB. The result is a thermodynamic description of the adsorption process regarding  $Q_{max}$  and  $K$  parameters for the two adsorbents. So, the difference in adsorption behavior can come either from a different nature of the sites via an increase in  $Q_{max}$ , or from a higher affinity for the adsorption sites via an increase of  $K$  value. Experimental adsorption isotherms at 298 K and the best fit of the suitable model are given for POS@PANI-ES and POS@PANI-EB in Figure 14. The thermodynamic parameters are given in Table 4. The Volmer model fitted more accurately the experimental



adsorption isotherm of PSP to POS@PANI-ES, whereas the Langmuir model was preferred for POS@PANI-EB. Therefore, the PSP molecules adsorbed on POS@PANI-ES are mobile because electrostatic adsorption prevails. Because electrostatic interactions are long-ranged, adsorbed PSP molecules are not necessarily at close contact to the cationic sites. PSP molecules can jump from one cationic site to another without having to overcome an energy barrier because the high density of cationic groups makes the sites being close each other and electrostatic interactions being non-localized. Conversely, adsorption on POS@PANI-EB takes place at well-defined sites, mostly the neutral quinone-diimine units. Adsorption requires a close contact of PSP molecules to these functional groups that behave as discrete independent binding sites, therefore meeting the assumptions of the Langmuir model. The thermodynamic modelling of adsorption onto POS@PANI-ES and POS@PANI-EB provided the parameters  $Q_{max}$  and  $K$  for the positively charged groups of PANI-ES and the quinone-diimine unit PANI-EB binding sites grafted onto the POS biomaterial. The binding affinity was higher for POS@PANI-ES due to the stronger interaction of PSP with the electrical charges of PANI-ES (mobile adsorption). This enhanced affinity is attributed to the anion exchange between the sulfonic group of PSP and chloride ions of the positively charged groups of the PANI-ES surface. The higher affinity of PSP compared to chloride may be attributed to its more hydrophobic nature. In contrast, the adsorption of PSP on POS@PANI-EB is driven by non-electrostatic interactions, coming from hydrogen bonding interactions between the quinone-diimine and amine groups of PANI-EB and the phenolic group of PSP, which can be considered localized adsorption sites.



**Figure 14.** Adsorption isotherms and best non-linear fits of the adsorption models (Red: Volmer model and Blue: Langmuir model) to experimental PSP adsorption (A): POS@PANI-ES and (B): POS@PANI-EB.

**Table 4.** Parameters of the best fits of the Volmer and Langmuir models to experimental adsorption isotherms of PSP to POS@PANI-EB and POS@PANI-ES at 298 K.

Models	POS@PANI-ES			POS@PANI-EB		
	Log(K)	$Q_{max}$ ( $\mu\text{mol}\cdot\text{g}^{-1}$ )	ARE	Log(K)	$Q_{max}$ ( $\mu\text{mol}\cdot\text{g}^{-1}$ )	ARE
Langmuir isotherm	2.57	43.5	0.09	3.89	37.8	0.03
Volmer isotherm	3.29	71.5	0.03	3.02	57.23	0.22

### 3.2.3. Comparison of adsorption capacities of different adsorbents.

In the field of wastewater treatment and environmental remediation, various bioadsorbents have been extensively studied for their efficacy in removing pollutants from aqueous solutions. Table 5 presents a comprehensive comparison of the adsorption capacities reported in the literature for different adsorbents. Activated carbon, a widely used adsorbent known for its high surface area and porous structure, demonstrates excellent adsorption capacities for organic pollutants [41,42]. Biomass wastes hold great promise due to their abundance, renewability, and cost-effectiveness. Their adsorption capabilities make them valuable candidates for sustainable and eco-friendly approaches to wastewater treatment. Among these, *Ficus carica* bast, the sea plant *Posidonia oceanica* L., and dead leaves of oak trees have shown notable adsorption capacities for various pollutants [43,44]. Agricultural by-products, such as corn silk, coconut shells, and rice husks, have gained attention due to their cost-effectiveness and abundant availability, exhibiting notable adsorption capacities for a range of pollutants [45–47]. These agricultural wastes have been utilized as renewable sources for the production of adsorbents, offering an alternative to traditional activated carbon. Moreover, food wastes, such as chicken eggshell beads, lemon peel, and almond shell, exhibit unique adsorption properties for both cationic and anionic dyes, showcasing their potential applications in environmental remediation [48–50]. The adsorption capacity of *Posidonia oceanica* L. coated with polyaniline emeraldine salt form is consistent with these diverse adsorbents, demonstrating its efficacy in the removal of pollutants from aqueous solutions.

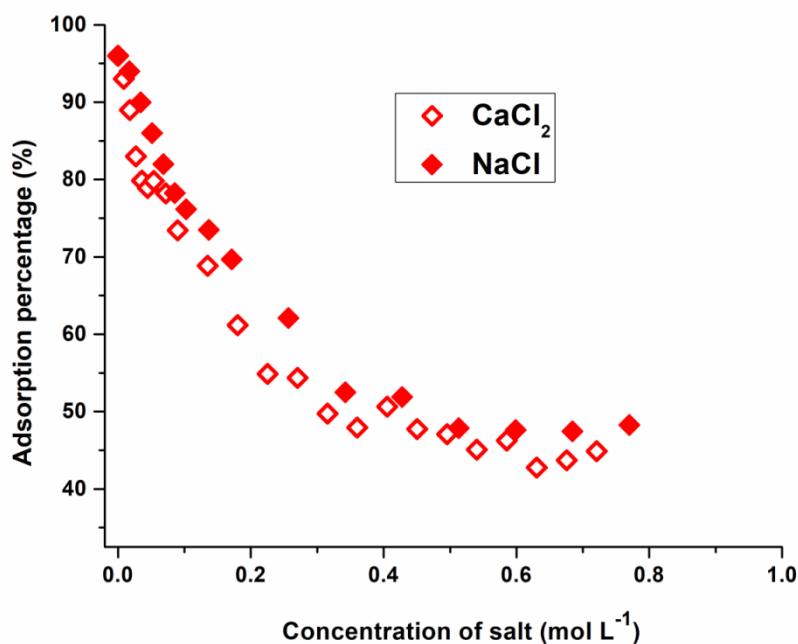
**Table 5.** Comparison of several adsorbent capacities for dye removals in aqueous solution.

Materials		Dyes	Adsorption capacity ( $\text{mg}\cdot\text{g}^{-1}$ )	Refs
Commercial materials	Activated carbon	Acid yellow 23	3.32	[41]
	Nano-activated carbon	Methylene blue	28.09	[42]
Biomass wastes	<i>Ficus carica</i> bast	Methylene Blue	55.56	[43]
	Sea plant ( <i>Posidonia oceanica</i> L.)	Methylene Blue	27.78	[44]

	Dead leaves of oak trees	Crystal violet	31.65	[44]
Agriculture wastes	Corn silk	Reactive blue 19	60.60	[45]
	Coconut Shells	Methylene Blue	106.40	[46]
	Rice Husks	Congo red	1.58	[47]
Food wastes	Chicken eggshell beads	Reactive blue 4.	24.10	[48]
	Lemon peel	Reactive blue 4	2.59	[49]
	Almond shell	Crystal violet	12.20	[50]

### 3.3. Effect of ionic strength

To investigate the influence of electrolytes in solution on the adsorption of PSP onto POS@PANI-ES, varying quantities of NaCl or CaCl<sub>2</sub> were introduced into the aqueous PSP solution with an initial concentration of  $C_0 = 0.25 \text{ mmol L}^{-1}$ . The presence of inorganic salts in the solution greatly decreases the adsorption of PSP, with the two salts exhibiting almost identical effects (Figure 15). The amount of PSP adsorbed goes from 96% in the absence of added salts to approximately 42% with an added ionic strength of  $0.40 \text{ mol L}^{-1}$ . Beyond  $0.40 \text{ mol L}^{-1}$ , the quantity of adsorbed PSP onto POS@PANI-ES remains constant. The observed reduction in PSP adsorption on POS@PANI-ES material in the presence of various electrolytes can be rationalized by competitive adsorption, where inorganic anions and PSP compete for surface sites on the adsorbent (40). Indeed, salts such as sodium chloride (NaCl) or calcium chloride (CaCl<sub>2</sub>) can disturb the favorable electrostatic interactions between the cationic polymer PANI and the PSP molecules. This competitive dynamic leads to a noticeable decrease in the accessibility of adsorption sites for PSPs, leading to an overall reduction in adsorption efficiency. In addition, the presence of salts can form an electrostatic barrier around adsorption sites, further undermining the interaction between the positive charges of the cationic polymer and the negative charges of the PSP molecules. These effects of ionic strength on the PSP adsorption process can pose a challenge when using POS@PANI-ES materials in water treatment. Indeed, these contain different salts that affect the adsorption capabilities of the materials. However, these materials can be affected by various salts which influence their adsorption capacities. Nevertheless, in water treatment scenarios, water is generally considered to have high salinity when the NaCl concentration is around  $0.06 \text{ mol L}^{-1}$  PSP remains approximately 80% adsorbed at this concentration, a level considered suitable for systems with robust adsorption capacities.



**Figure 15.** Adsorbed fraction of PSP onto POS@PANI-ES material in the presence of NaCl and CaCl<sub>2</sub> salts; initial concentration of PSP  $C_0 = 0.25 \text{ mmol L}^{-1}$ .

#### 4. CONCLUSION

The adsorption properties of phenol red dye on Posidonia surface-modified with polyaniline emeraldine salt, prepared by oxidative copolymerization in acidic medium, were compared with those of Posidonia grafted with polyaniline emeraldine base. Favorable performances of such material were revealed as fast adsorption kinetics and high adsorption efficiency for PSP. The simple comparison of adsorbed amounts of PSP molecule showed that both POS@PANI-ES and POS@PANI-EB materials could bind more PSP than the unmodified Posidonia. Modeling the adsorption isotherm allowed to separate the affinity contributions of the polyaniline sites for PSP. The data from the isothermal experiments of POS@PANI-EB fit well with the Langmuir model, which takes into account the presence of a localized type of adsorption sites, while the adsorption on POS@PANI-ES was in agreement with the Volmer model, which takes into account the mobility of the adsorbate at positively charged sites of the polyaniline salt. The presence of inorganic salts significantly affects the adsorption of PSP on POS@PANI-ES. Competitive adsorption between ions and PSP, in addition to disrupted electrostatic interactions caused by salts, leads to reduced adsorption efficiency. While this underscores the importance of considering ionic strength, the promising performance of POS@PANI-ES materials in water treatment is evident within an optimal salinity range. This highlights their potential as versatile and effective adsorbents to address water pollution challenges.

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**Author contributions.** All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by [Karima Ferchichi], [Amaini Chouchene], [Noureddine Amdouni], [Yves Chevalier] and [Souhaira Hbaieb]. The first draft of the manuscript was written by [Karima Ferchichi] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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