

Article

Nanocomposite-Based Aminated Polyethersulfone and Carboxylate Activated Carbon for Environmental Application. A Real Sample Analysis

Noof A. Alenazi ¹, Mahmoud A. Hussein ^{1,2,*} , Khalid A. Alamry ^{1,*} and Abdullah M. Asiri ^{1,3}

¹ Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia; noof0988@hotmail.com (N.A.A.); ceamr3@gmail.com (A.M.A.)

² Polymer Chemistry Lab., Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

³ Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

* Correspondence: maabdo@kau.edu.sa or mahmali@aun.edu.sa (M.A.H.); kaalamri@kau.edu.sa (K.A.A.)

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Abstract: Aminated polyethersulfone (PES–NH₂) has been synthesized and used with carboxylated activated carbon (AC–COOH) as an adsorbent using two different methods: in situ and ex situ techniques. The chemical modification of polyethersulfone (PES) to introduce –NH₂ functions was used to overcome the hydrophobicity of PES which maximizes its use in water treatment applications whereas applying AC–COOH to this polymer provides a promising effective method as an adsorbent-separation technique to remove dye pollutants from wastewater. The structure and characterization of aminated polyethersulfone with carboxylated activated carbon (PES–NH₂–AC–COOH) were identified using proton nuclear magnetic resonance (¹H-NMR), Fourier transform infrared (FT-IR spectroscopy), X-ray diffraction (XRD), thermal analysis (TA), and a scanning electron microscopy (SEM). The performance of PES–NH₂ in situ and ex situ with AC–COOH was tested for the adsorption of cationic (methylene blue) and anionic (acid red 1) dyes from an aquatic environment. The results of the study showed a better thermal stability for the PES–NH₂ with 20% AC–COOH with both in situ and ex situ techniques as well as an excellent adsorption performance in comparison with the bare PES–NH₂. The resultant polymers displayed significantly high adsorption rates for the acid red dye (60% and 68%) and methylene blue dye (61% and 88%) by PES–NH₂ with AC–COOH using in situ and ex situ techniques, respectively, in comparison with the control (PES–NH₂) which showed lower adsorption rates for both dyes (21% for acid red and 33% for methylene blue). Lastly, the study experimental measurements found the most suitable model to describe the kinetic behavior of the acid red dye adsorption by our developed polymer (by PES–NH₂ with AC–COOH) to be the pseudo-second-order kinetic model.

Keywords: dye adsorption; ex situ and in situ techniques; adsorptive behavior; activated carbon; nanocomposites

1. Introduction

Pollutants including heavy metals (mercury, cadmium, lead, chromium, etc.) and organic compounds (including dyes, personal care products, and pharmaceutical substances) are considered hazardous contaminants when they reach water streams for both human and living organisms [1]. Among all these pollutants, dyes are considered one of the most persist pollutants in water due to its low degradation and high stability in the aquatic environment. Dyes have two fundamentals parts: chromophores, which are responsible for their colors, and auxochromes, which are responsible for their binding affinity towards fibers [2,3]. Dyes are commonly used in food, textile, pharmaceutical,

cosmetic, and papers productions. In the textile sector, almost 200,000 tons of dye is lost as wastes during the dying processes for the textile synthesis [4]. Most of these waste dyes present in the aquatic environment for a long time due to their high stability to light and temperature. The high demand for the textile products leads to a high demand for synthetic dyes, and wastewaters contaminated with dyes are considered one of the most significant causes for pollutions in the aquatic environment. Additionally, synthetic dyes are considered a great risk because they are highly toxic to the aquatic environment and are carcinogenic to humans. More specifically, azo dyes have been discovered to have mutagenic effects because of their biotransformation derivatives once they enter the body by digestion. The biotransformation of azo dyes occurs via the liver enzymes to form *N*-hydroxylamine compounds, which have been found to cause damage to DNA. Additionally, dyes have been linked to many health illness issues related to kidneys, brain, liver, as well as central nervous and reproductive systems [4,5]. There are different techniques to remove these dyes from wastewater including adsorptions techniques. The adsorption method is known to be the most effective and low-cost methods, and there are different types of adsorbents including fly ash, lignite, activated carbon black (AC), sawdust, coal, and wood [6]. Activated carbon is often used as an adsorbent due to its variability and low cost [6,7]. However, in order to enhance the use of AC as adsorbents, AC particles should be used with polymeric materials [8,9].

Polyethersulfone (PES) is a well-known polymer that has been applied to various adsorbents-separation techniques including dyes adsorption [6] and other organic compounds adsorption [8]. This wide use of PES is because of its high thermal, mechanical, and chemical properties [4]. However, the hydrophobicity of PES is considered one of the drawbacks that limit its use. The additional of hydrophilic functions to PES (including amino, carboxylic, sulfonic, and so forth) could be an effective method to overcome its hydrophobicity [10]. In this work, PES has been chemically modified to PES-NH₂ in order to improve its hydrophobicity. The structure PES-NH₂ was confirmed using proton nuclear magnetic resonance (¹H-NMR) and Fourier transform Infrared (FT-IR) spectroscopy. The AC-COOH fine particles were then fabricated in our lab and they have been used with PES-NH₂ using two methods: the in situ and ex situ techniques. Then, the PES-NH₂ with AC-COOH structures were identified and characterized using FT-IR spectroscopy, X-ray diffraction analysis (XRD), thermal analysis (TA), and scanning electron microscopy (SEM) technique. The performance of PES-NH₂ in situ and ex situ with AC-COOH was tested in order to examine its performance in removing both cationic (methylene blue) and anionic (acid red 1) dyes from the aquatic environment. Because of its high adsorption capacity (q_e) in comparison with methylene blue, an acid red dye was used to test the adsorption capability of the solid phase (SP) of PES-NH₂-AC-COOH under different parameters including pH, contact time, and temperature. Then, the kinetics behaviors and thermodynamic characteristics of acid red adsorption onto PES-NH₂ in situ and ex situ with AC-COOH were further studied. Finally, two real environmental samples from the Red Sea and tap water were spiked with acid red and used to explore the environmental applications of PES-NH₂ in situ and ex situ with AC-COOH in removing the acid red dye from the aqueous environment.

2. Experimental

2.1. Materials

All chemicals and solvents were used as they were obtained from their companies with no purification. The polyethersulfone (PES) was purchased from Solvay Chemicals Limited, Panoli, India. The deuterated dimethylsulfoxide (DMSO-d₆) (99.8%), chloroform (99.8%), dichloromethane (DCM) (99.8%), and acid red were purchased from the Sigma-Aldrich Company, Milwaukee, WI, USA. The potassium iodide (KI), sodium hydroxide (NaOH), Tin (II) chloride (SnCl₂), hydrochloric acid (HCl) (37%), sulfuric acid (H₂SO₄) (95–97%), and nitric acid (HNO₃) (65%) were all obtained from BDH Ltd., Poole, UK. For the preparation of standard and stock solutions, the deionized water was purchased from Millipore Milli-Q Plus, Milford, MA, USA.

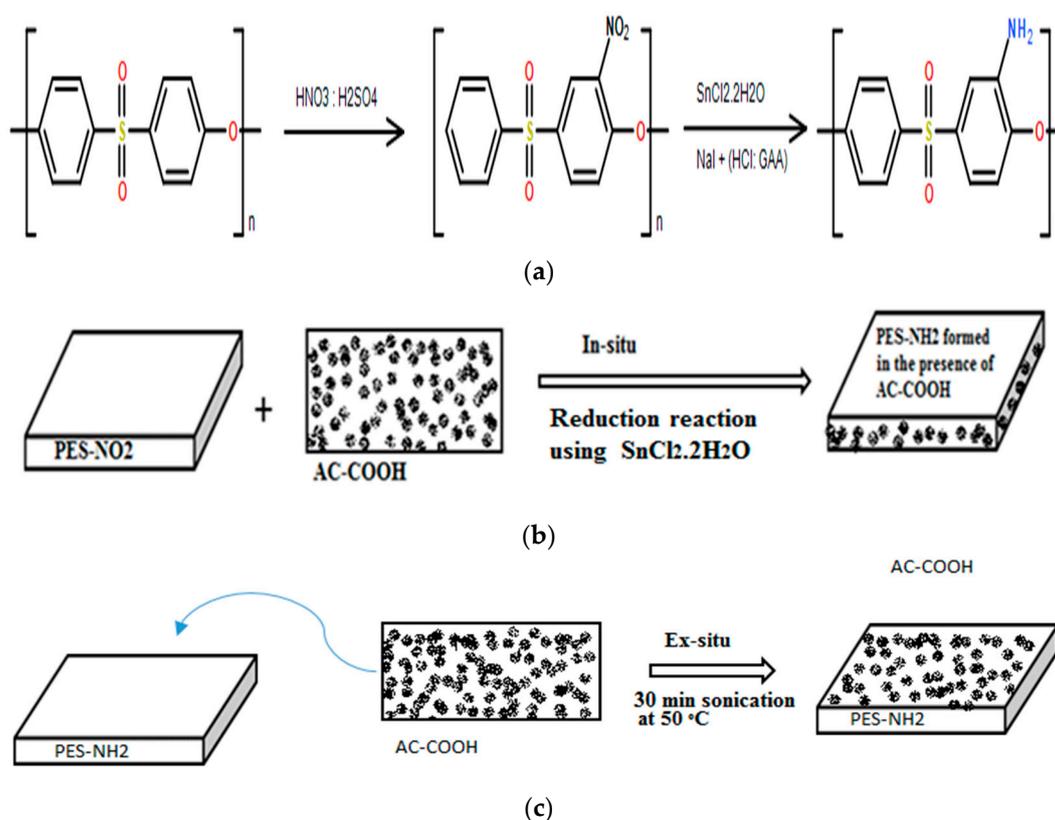
2.2. Reagents

Acid red was prepared with 1000 $\mu\text{g}/\text{mL}$ as a stock solution. The stock solution was further diluted to 10–100 $\mu\text{g}/\text{mL}$ using fresh deionized water. Britton–Robinson buffer (BR) with pH of 2 to 11 and HCl solution of 0.1 mol/L were prepared in order to be used as extraction solvents during the acid red adsorption utilizing the polymer solid phase (SP) technique.

2.3. Methods

2.3.1. Synthesis of PES–NH₂

PES–NH₂ was prepared with two steps process reactions, a nitration reaction followed by a reduction reaction, following a procedure done by Haider et al. [11] as shown in Scheme 1a. First for the nitration reaction, 2 g of PES was added to a mixture of 25 mL (H₂SO₄) and 10 mL of (HNO₃) at 65 °C for 5 h. Then, the reaction mixture solution was ended by pouring the reaction solution into an ice bath filled with cold deionized distilled water (D.D.W). The solution was then filtered and washed with NaOH (2 M) and several times with D.D.W. Finally, the PES–NO₂ particles were then dried at a temperature of 30 °C for two days. For the reduction step, 2 g of PES–NO₂ were suspended in 25 mL of chloroform in a three neck rounded flask attached with condenser. An amount of 25 g of SnCl₂ and 1.67 g KI were suspended in 100 mL of a mixture of HCl. Glacial acetic acid (GAA) (2:1) was then added slowly to °C PES–NO₂ solution at 65 °C. The reaction mixture solution was then continued at a temperature of 65 °C for 6 h. Finally, the reaction solution was left at room temperature to cool the solution down and it was then poured into a NaOH (2 M) bath, filtered, and washed with D.D.W for several times until the pH became around 8 to 7. The PES–NH₂ particles were obtained and dried at 30 °C for two days.



Scheme 1. The preparation of PES–NH₂ (a), PES–NH₂ in situ with AC–COOH inside the polymer matrix (b), and PES–NH₂ ex situ with AC–COOH onto the polymer matrix surface (c).

2.3.2. Preparation of AC-COOH

AC-COOH was fabricated, the carboxylic functional groups introduced to the surface of AC, following a procedure done by Marwani et al. [12]. In this work, 5 g of AC was suspended in 150 mL of HNO₃ with a concentration of 32.5% (v/v) under stirring and heating at 60 °C for 5 h. The resultant particles were filtered and washed with deionized distilled water (D.D.W). Then, the AC-COOH particles were dried using an oven vacuum set at a temperature of 80 °C for 8 h.

2.3.3. Preparation of PES-NH₂ with PES with AC-COOH by the In Situ Technique

For PES-NH₂ in situ with AC-COOH, different concentrations of AC-COOH (2, 5, 10, and 20 wt %) were added to 2 g of PES-NO₂ prior to the synthesis of PES-NH₂ as shown in Scheme 1b. This approach was explored because of its simplicity and the high dispersion capability of AC-COOH particles inside the polymer matrix. The drawback of this approach is that AC-COOH particles could have less reactivity than the ex situ technique with pollutants.

2.3.4. Preparation of PES-NH₂ with AC-COOH by the Ex Situ Technique

An amount of 2 g of PES-NH₂ particles was suspended first in DCM for 5 min at 50 °C in an ultrasonic bath with different concentrations of AC-COOH (2, 5, 10, and 20 wt %). Then, the mixture was sonicated with an ultrasonic probe for 30 min. The mixture transferred into a glass supporting surface and dried at room temperature for 1 day as shown in Scheme 1c. This approach is used because it is more applicable for large-scale applications than in the situ method, and the ex situ method allowed the direct interactions of AC-COOH particles with pollutants that were present in the wastewaters. The drawback of this approach is that the AC-COOH particles have less stability in the polymeric matrix than in the in situ method.

2.4. Techniques

The spectrophotometric measurements were acquired using a spectrophotometer of a Perkin-Elmer UV-Visible (Lambda 25 model from the USA) with a UV range of 190–1100 nm equipped with quartz cell (10 mm as path width). For the pH test solution and measurements, a pH Orion meter (EA 940 model) was used. The FT-IR spectra were obtained with a range of 4000 cm⁻¹–450 cm⁻¹ wavenumbers using a Nicolet (6700) FT-IR Spectrometer from the Thermo Electron Corporation. ¹H-NMR analysis was acquired in DMSO-d₆ on a Bruker DPX 600 MHz spectrometer using tetramethylsilane (TMS) as the internal standard at room temperature. For the XRD analysis, powder XRD data were achieved utilizing an electronic Philips diffractometer (PW 103/00 model) equipped with radiation of Ni-filtered Cu K α , in which the range of 2 θ is 5°–80°. For the SEM analysis, the morphology of the PES-NH₂ and PES-NH₂-AC-COOH was examined by a SEM using Quanta, FEI.

2.5. Adsorption Technique for Dyes

An amount of 0.02 g of PES-NH₂ with AC-COOH ex situ and PES-NH₂ with AC-COOH in situ were measured in a 20 mL solution containing both acid red with a concentration of 20 mg/L and HCl with a concentration of 0.1 mol/L, and then the solution was shaken for 1 h using a shaker device. Then, the supernatant was separated from the solid residues and taken up in order to be photometrically measured with respect to a blank sample [13]. The adsorption of acid red was calculated by subtracting the absorption of acid red before (A_b) from the absorption of acid red after (A_f) it was adsorbed by the polymer solid phase. The calculations of the percentage of sorption (% E), the acid red retention (q_e) at equilibrium/mass of the solid sorbent (g/mol), as well as the coefficient of distribution (K_d) for the adsorbed acid red onto the PES-NH₂ with AC-COOH were all determined as they were described previously [13]. Three repeated measurements were done for K_d and %adsorption, and the average values were taken in which the precision differed \pm 2% only. The effect of the shaken

time, as well as temperature for the acid red retention on PES-NH₂ with AC-COOH solid sorbents, were investigated in detail.

2.6. Environmental Applications and Sample Collection

Water samples from the Red Sea and tap water were collected in order to assess the performance of PES-NH₂ with AC-COOH solid sorbents for the acid red adsorption and recovery. The Red Sea water sample used in this study was collected from the Jeddah coast in Saudi Arabia whereas the tap water was obtained from the chemistry labs at the King Abdul-Aziz University, Jeddah city, Saudi Arabia. The samples were filtered through a membrane filter with 0.45 µm and the samples then preserved with Teflon bottles in a dark area with a temperature of 5 °C. Samples of 100 mL were pH modified to a pH of 1 using an HCl solution that had a concentration of 0.1 mol/L and then they were passed through the polymer solid phase. Then, the recovered acid red was calculated spectrophotometrically.

3. Results and Discussions

3.1. Characterization of PES-NH₂ with AC-COOH

¹H-NMR was used to confirm the chemical structure of PES, PES-NO₂, and PES-NH₂, respectively as shown in Figure 1. According to ¹H-NMR of the PES spectrum, two distinct doublet peaks were noticed at 7.9 ppm and 7.2 ppm accounting for two protons (a and b), respectively. After nitration, the ¹H-NMR of PES-NO₂ spectrum showed three distinct peaks. The first peak was a doublet at 7.7 ppm (c) because of the ortho coupling for the proton that appeared at 8.8 ppm. The second distinct peak which appeared at 8.4 ppm (d) was a doublet of the two doublets of the protons that were ortho and meta coupled (at 8.8 ppm and 7.7 ppm, respectively), which suggested that the nitration of PES had occurred. The third peak, which appeared at 8.8 ppm (e), was a doublet because of the proton that showed meta coupling as shown in Figure 1. Therefore, it can be concluded that the nitration occurred at the carbon that was on the ortho position to the ether oxygen. After the reduction of PES-NO₂, the ¹H-NMR of PES-NH₂ spectrum showed four distinct peaks that were shifted to a lower field because of the donating electron nature of the amine, unlike the nitro functions which have an electron withdrawing nature. The first peak of the four amine peaks was a single peak and it was noticed at 5.5 ppm rising from the amine protons. The second peak was noticed as a doublet at 6.8 ppm and this is because of the presence of the proton that showed ortho coupling. The third distinct peak was a doublet of doublets at 6.9 ppm because of the two protons that showed ortho and meta couplings. Lastly, the fourth peak was noticed as a doublet at 7.2 ppm and this is because of the presence of the proton that showed meta coupling. This ¹H-NMR data were in agreement with the previous reported data [14].

The chemical structures of PES, PES-NO₂, and PES-NH₂ were further confirmed using FT-IR spectroscopy as shown in Figure 2. The chemical structure of the PES contains three important functions including benzene, ether, and sulfone. The presence of benzene rings should exhibit three peaks in the range of 1600 cm⁻¹ to 1400 cm⁻¹, and, in the PES spectrum, the three peaks were observed at 1576 cm⁻¹, 1483.7 cm⁻¹, and 1405 cm⁻¹. The presence of the ether function was confirmed due to the presence of its two stretching peaks at 1319 cm⁻¹, as well as 1296 cm⁻¹. The two stretching peaks indicating the presence of the sulfone group were also noticed at 1144 cm⁻¹ and 1100 cm⁻¹. Our data of the PES spectrum came in agreement with previously reported studies on PES FT-IR analysis [12,15]. The FT-IR spectrum of PES-NO₂ showed an asymmetric peak at 1531 cm⁻¹ and a symmetrical peak at 1342 cm⁻¹ which indicate the attachment of the -NO₂ functions on the PES. After the reduction of the -NO₂ groups to -NH₂ groups, the FT-IR of PES-NH₂ spectrum exhibited the formation of -NH₂ by showing two peaks at 3344 cm⁻¹, as well as 3451 cm⁻¹, and the deformation of -NH₂ by showing a peak at 1622 cm⁻¹. This confirms the attachment of the amine functions on PES. Both our FT-IR of the PES-NO₂ and PES-NH₂ spectra came in agreement with a previously reported study [12]. The FT-IR spectra of PES-NH₂ with different concentrations of AC-COOH using the in situ and ex situ techniques are shown in Figure 3a,b, respectively.

In Figure 3a, it can be clearly seen that as the concentrations of AC-COOH increased, the shifting of the amine stretching peaks was noticed, which suggests that the interactions between AC-COOH and PES-NH₂ were formed. In addition, it was also noticed that the effects of increasing the concentrations of AC-COOH in PES-NH₂ resulted in overlapping peaks between the amine and -OH for the acid peaks until it became one peak at 3354 cm⁻¹ for using 10 wt % of AC-COOH and at 3367 cm⁻¹ for using 10 wt % of AC-COOH instead of two peaks for the amine functions. We suggest that the noncovalent interactions such as intermolecular forces, dipole-dipole, hydrogen bonding, and Van der Waals interactions between AC-COOH and PES-NH₂ took place during the synthesis of the polymer through the in situ technique. However, when the PES-NH₂ was coated with AC-COOH on its surface through the ex situ technique, the noncovalent interactions were weaker, which explained the FT-IR spectrum in Figure 3b, in which less shifting was seen between the amine stretching peaks during the presence of AC-COOH on the surface of the PES-NH₂.

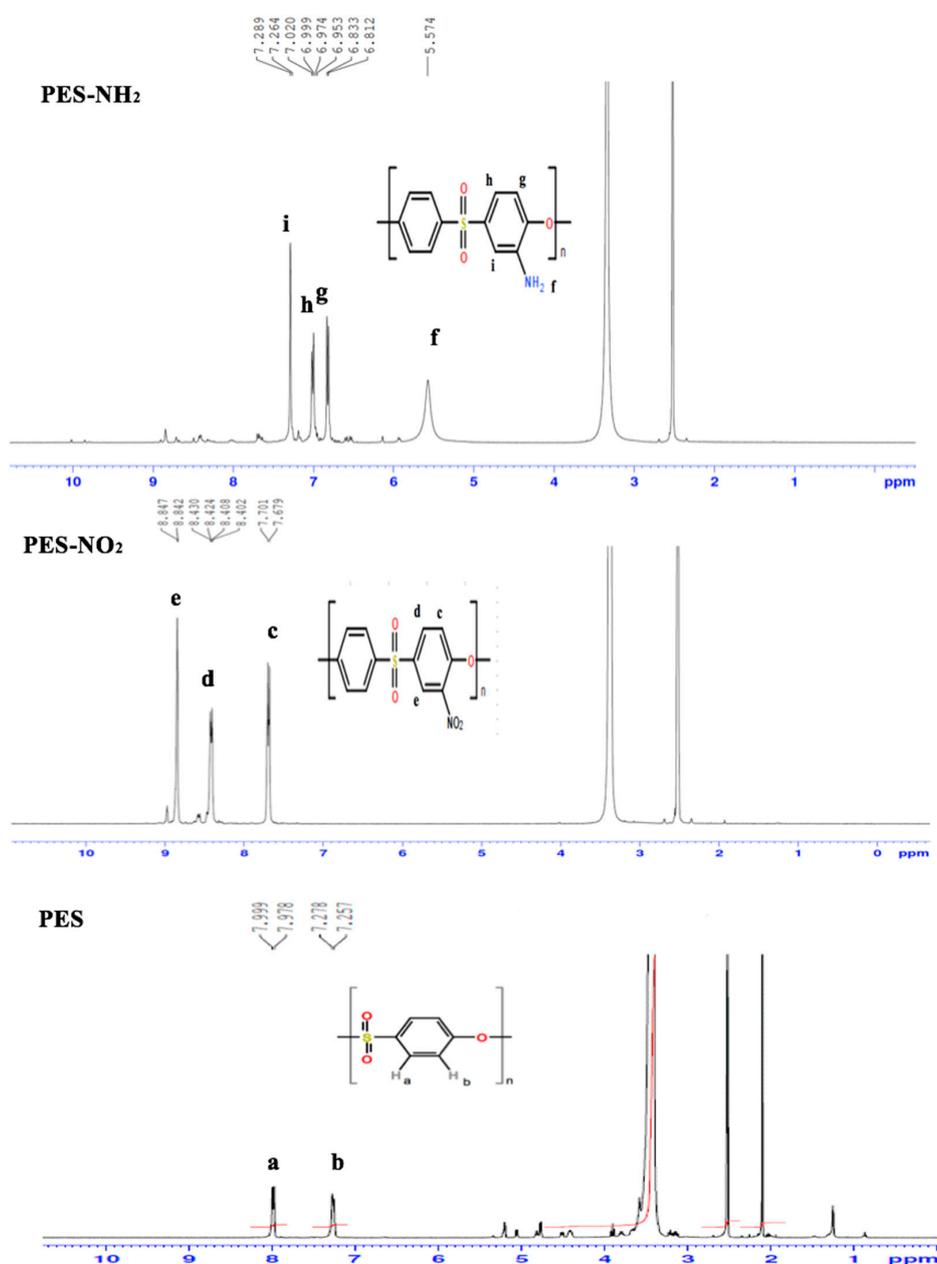


Figure 1. The ¹H-NMR of PES, PES-NO₂, and PES-NH₂.

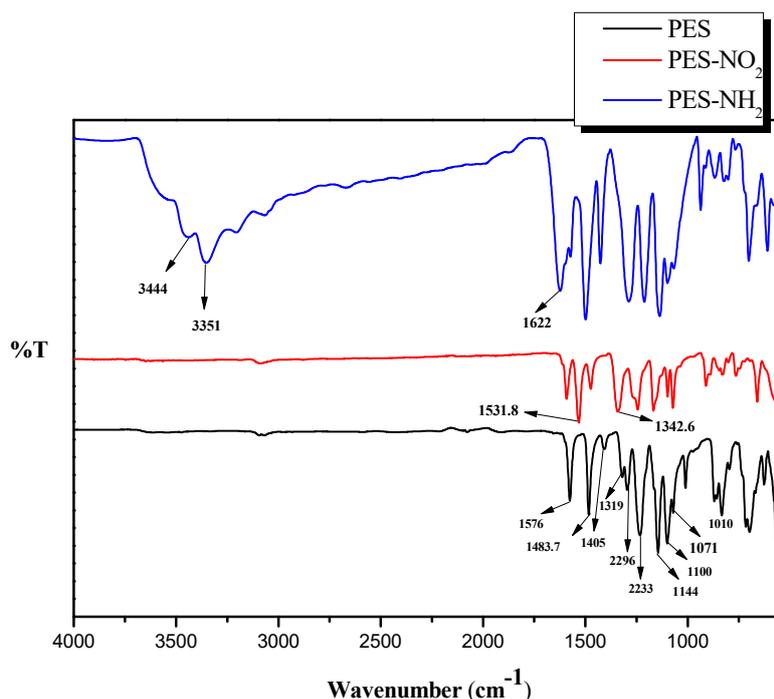


Figure 2. The FT-IR spectrum of PES, PES-NO₂, and PES-NH₂.

The XRD data confirmed the chemical compositions of the plan PES-NH₂ versus the PES-NH₂ in situ and the PES-NH₂ ex situ with AC-OOH, as shown in Figure 4a,b, respectively. In Figure 4a, the PES-NH₂ has an amorphous structure due to the presence of the benzene rings and the ether bonds, which show a broad peak at $2\theta = 21^\circ$ that came in agreement with previous data reported [12,15]. Two broad peaks appeared after blending the PES-NH₂ with AC-OOH at $2\theta = 33^\circ$ and 52° , which referred to the presence of AC-COOH and their interactions with PES-NH₂, observed from the XRD data. The XRD data of PES-NH₂ with AC-COOH in the ex situ technique did not show any change in the structure as shown in Figure 4b, in which all the resultant polymers showed only one broad peak at $2\theta = 21^\circ$, which is identical to the plan polymer. This suggests that PES-COOH was coated only on the surface of PES-NH₂, which appeared in XRD as one peak since no internal interaction was formed between the polymer and AC-COOH particles.

The thermogravimetric analysis (TGA) of the PES-NH₂ (control), as well as PES-NH₂ in situ and ex situ with AC-COOH, was performed with a heating rate at $10^\circ\text{C}/\text{min}$ and under nitrogen flow. The TGA curves of PES-NH₂ with different concentrations of AC-COOH underflow through the in situ technique appeared to be different from the plan PES-NH₂ curve as shown in Figure 5a, whereas Figure 5b shows the derivative thermogravimetric (DTG) analysis for the maximum weight loss. The differences of these curves are because there were variations in the chemical structures between the control (PES-NH₂) and PES-NH₂ with 2%, 5%, 10%, and 20% of AC-COOH using in the in situ method caused by the noncovalent strong interactions, which, in turn, also seem to decompose differently as they appeared in Figure 5a. As the concentration of activated carbon increases, a better thermal stability was noticed as shown in Table 1. The maximum weight loss in the control was at 320°C whereas the PES-NH₂ with 20% AC-COOH was at the higher temperature of 340°C . In addition, the control was decomposed (T_{50}) at a lower temperature, around 529°C , while the decomposition of the PES-NH₂ with 20% AC-COOH was improved to be at 839°C . The thermal stability of the PES-NH₂ in situ with 20% AC-COOH improved significantly in comparison to the control (Table 1). The strong interactions formed during the synthesis between AC-OOH and PES-NH₂ have an impact in increasing the thermal stability of the polymer, which was in agreement with a previous study [16], whereby an increase in the thermal stability of the activated carbon occurred when it was blended with cellulose acetate versus the thermal stability of activated carbon only.

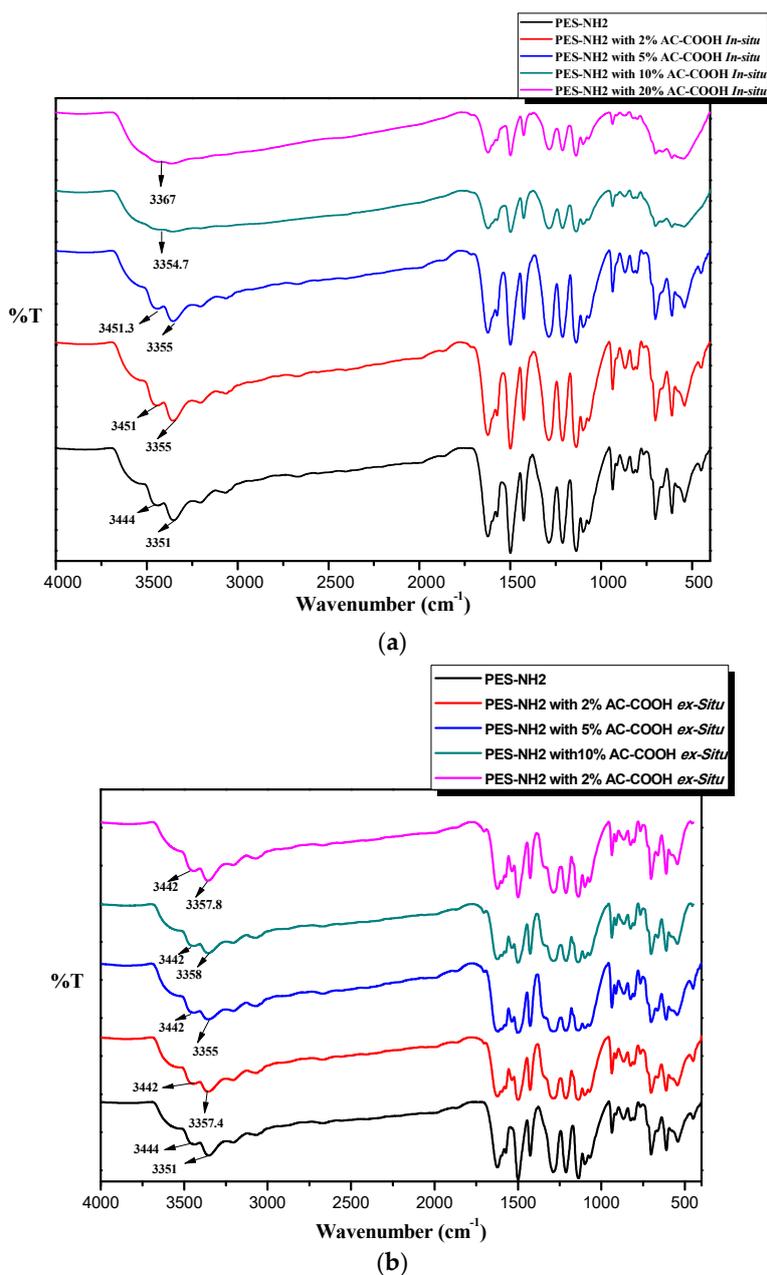


Figure 3. The FT-IR spectrum of PES-NH₂ versus PES-NH₂ with 2%, 5%, and 10% of AC-COOH using the (a) in situ and (b) ex situ techniques.

Table 1. The thermal behavior of PES-NH₂ with AC-COOH using the in situ technique.

Products	CDT _{max} ^a (°C)	CDT _{Final} ^b (°C)	Temperature (°C) for Various Percentage Decompositions ^b		
			T ₁₀	T ₂₅	T ₅₀
PES-NH ₂ (control)	320	850	293	331	529
PES-NH ₂ with 2% AC-COOH	333	850	298	339	676
PES-NH ₂ with 5% AC-COOH	338	850	224	359	647
PES-NH ₂ with 10% AC-COOH	340	850	128	435	800
PES-NH ₂ with 20% AC-COOH	340	850	127	551	839

^a Determined from the DTG curves. ^b The values were determined by the TGA at a heating rate of 10 °C·min⁻¹.

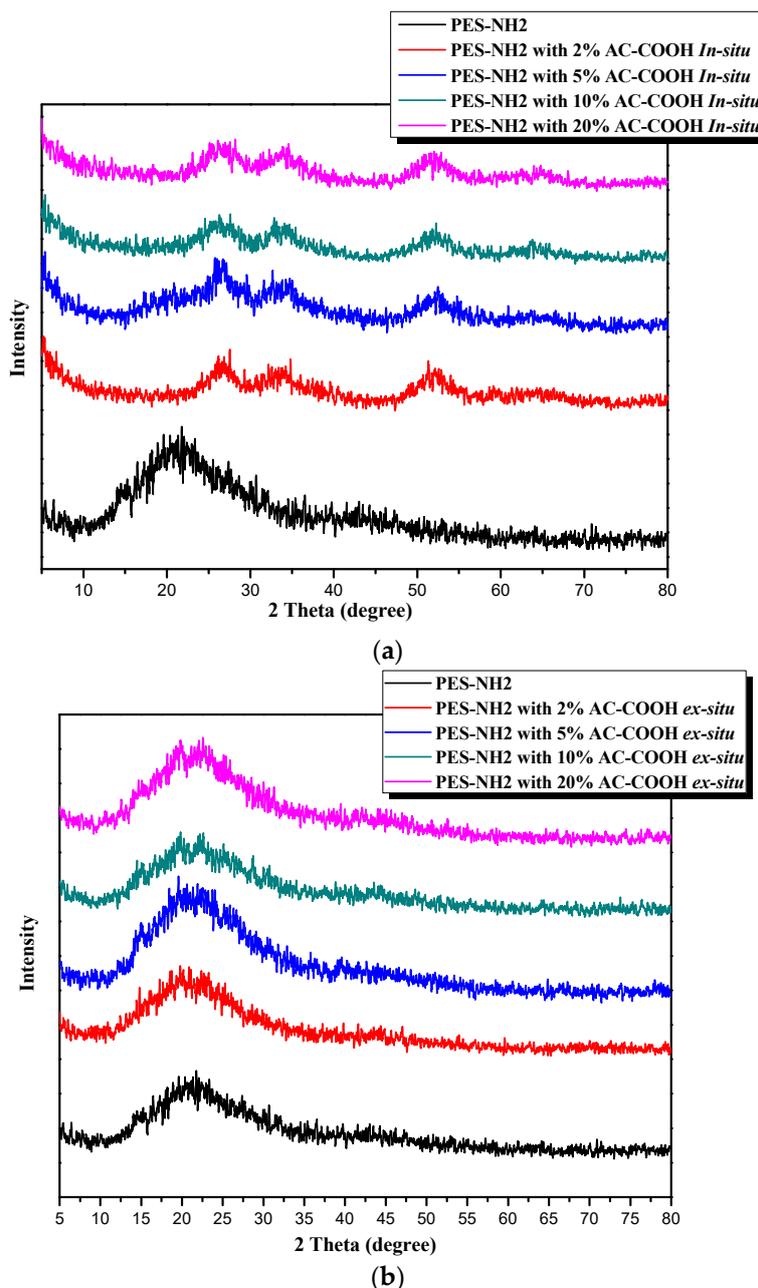


Figure 4. The XRD of PES-NH₂ with 2%, 5%, and 10% of AC-COOH with 2%, 5%, 10%, and 20% of AC-COOH in the (a) in situ and (b) ex situ methods.

On the other hand, the addition of AC-COOH to PES-NH₂ using the ex situ method, as shown in Figure 5c,d, improved the thermal stability in a way less than in the in situ method, but with a higher thermal stability in comparison to with the control. This came in agreement with the XRD data, which showed a slight change in the chemical structures between the control and the PES-NH₂ with AC-COOH by the ex situ method. Table 2 shows the enhancement of the thermal stability of the PES-NH₂ ex situ with AC-COOH in which the temperature of the maximum weight loss was 337 °C for the addition of 20% of AC-COOH to the PES-NH₂ whereas it was only 320 °C for the control. The decomposition of half the weight of the polymer (T_{50}) was only 534 °C for the control while it was 677 °C for the PES-NH₂ ex situ with 20% AC-COOH.

Table 2. The thermal behavior of PES-NH₂ with AC-COOH using the ex situ technique.

Products	CDT _{max} ^a (°C)	CDT _{Final} ^b (°C)	Temperature (°C) for Various Percentage Decompositions ^b		
			T ₁₀	T ₂₅	T ₅₀
PES-NH ₂ (control)	320	850	314	336	534
PES-NH ₂ with 2% AC-COOH	331	850	314	355	555
PES-NH ₂ with 5% AC-COOH	333	850	313	355	518
PES-NH ₂ with 10% AC-COOH	337	850	307	346	605
PES-NH ₂ with 20% AC-COOH	337	850	303	346	677

^a Determined from the DTG curves. ^b The values were determined by TGA at the heating rate of 10 °C·min⁻¹ under the nitrogen flow.

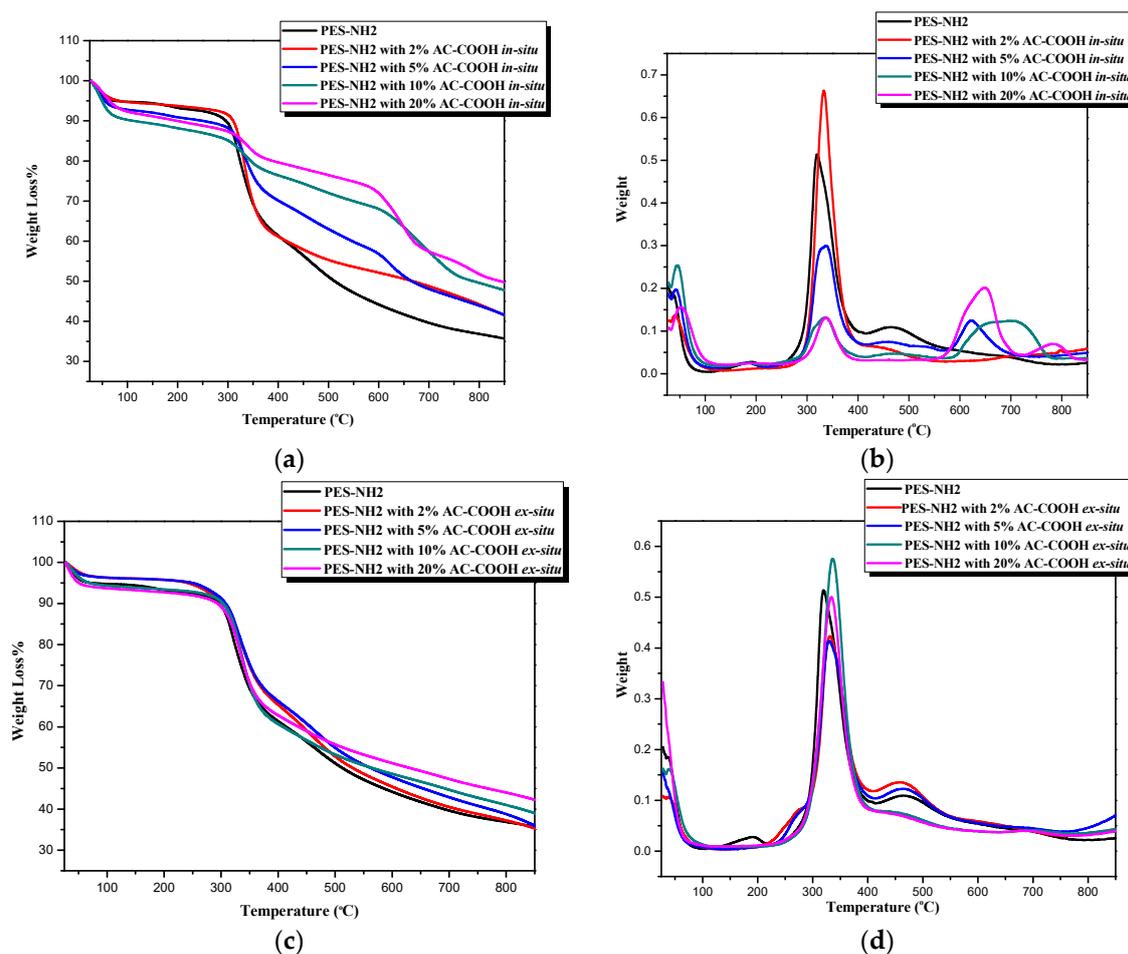


Figure 5. The TGA and DTG curves of PES-NH₂ (control) versus PES-NH₂ with different concentrations of AC-COOH in the in situ technique: (a,b); and the ex situ technique: (c,d).

The morphology of PES-NH₂ versus the PES-NH₂ with 10% AC-COOH in situ and ex situ are shown in Figure 6 on both the micro- and nanolevels. The SEM images show that PES-NH₂ (control) and the structural features of the PES-NH₂ with AC-COOH ex situ are similar, while the PES-NH₂ with AC-COOH in situ are different. The SEM images exhibited aggregations in the particles of PES-NH₂ with AC-COOH in situ, which clearly indicates that the in situ technique alters the morphological structure of the polymer unlike the ex situ method, which did not show any noticeable change on the morphology of PES-NH₂ in comparison with the control.

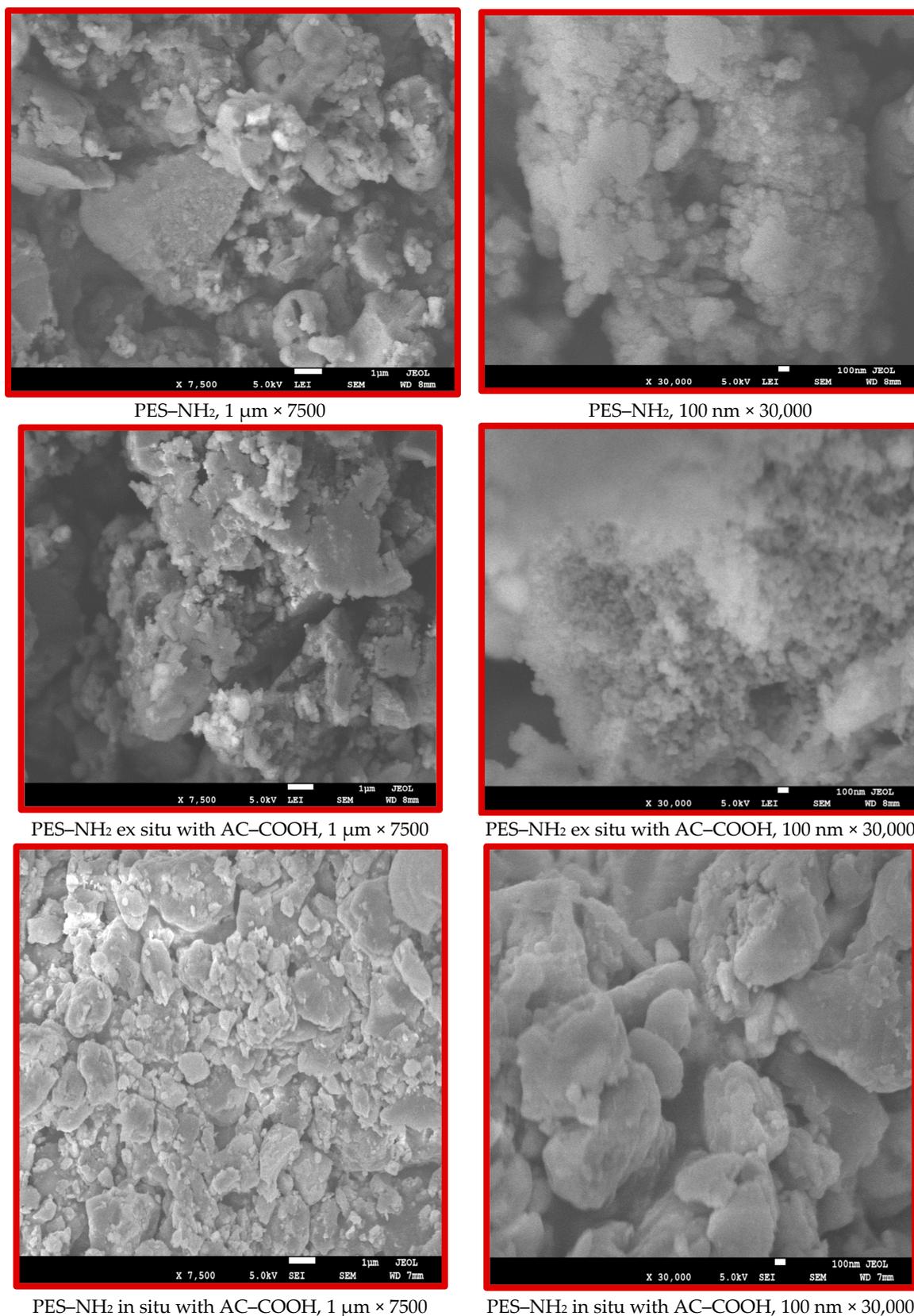


Figure 6. The SEM of only the PES-NH₂, the PES-NH₂ with the AC-COOH ex situ, and the PES-NH₂ with AC-COOH in situ.

3.2. The Performance of PES-NH₂ with AC-COOH in Dyes adsorption

The performance PES-NH₂ in situ and ex situ with AC-COOH for the adsorption of dyes has been examined. In this work, acid red 1, an anionic dye, was used to test the capabilities of these polymers to adsorb it from aqueous solutions (Figure 7a). As shown in Table 3, as the concentration of AC increased in both techniques, a remarkable increase in the acid red dye adsorption was observed while the control polymer showed the lowest adsorption with only 21% in comparison with the PES-NH₂ in situ and ex situ technique with 20% AC-COOH, which showed 58% and 61% adsorption, respectively. Because PES-NH₂ with 20% AC-COOH gave the highest percentage of adsorption results in both techniques, these polymers were tested further with methylene blue (Table 4) which is a cationic dye, to examine the performance of these polymers with cationic dyes. As shown in Table 4, PES-NH₂ with 20% AC-COOH ex situ gave an 88% adsorption for methylene blue (5 ppm) in comparison with 60% for acid red (20 ppm). In addition, PES-NH₂ with 20% AC-COOH in situ showed 68% for methylene blue (5 ppm) and 60% for acid red (20 ppm) in comparison with the control PES-NH₂ that gave 1.6% only for methylene blue (5 ppm) and 21% for acid red (20 ppm).

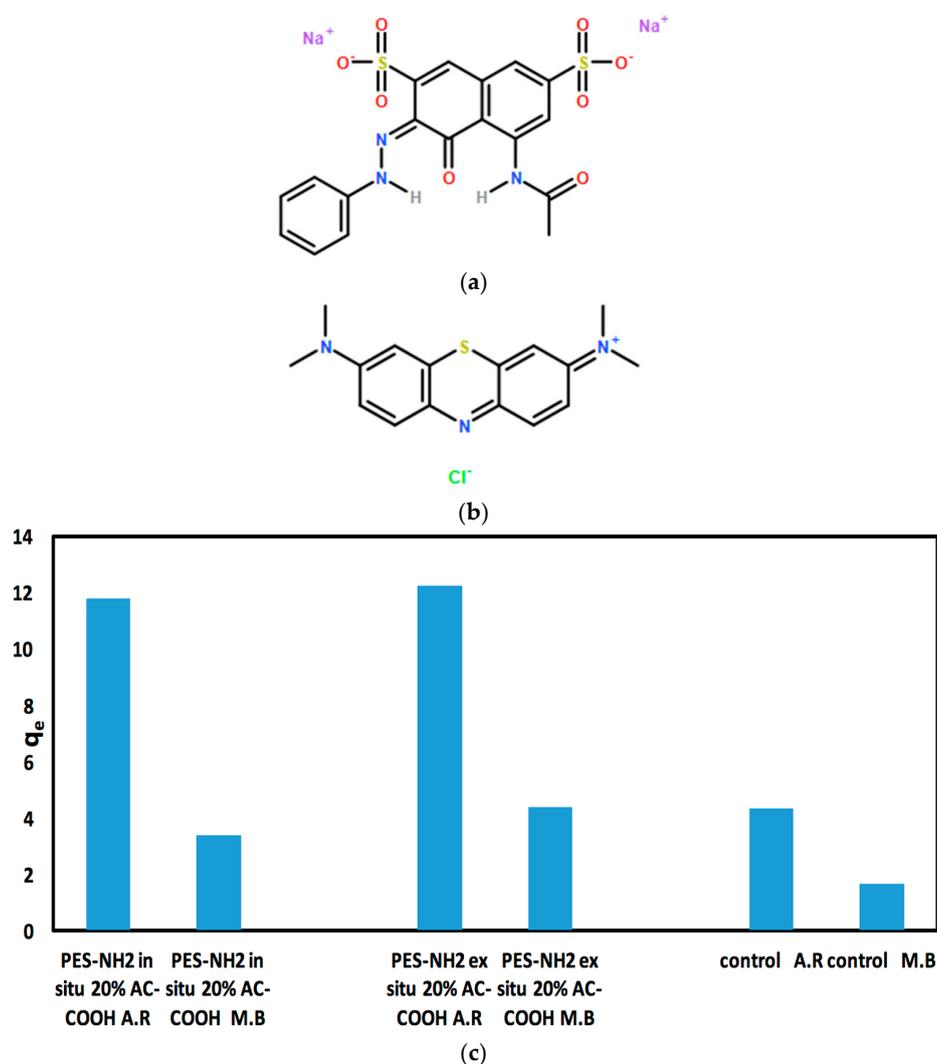


Figure 7. The chemical structure of acid red 1 (a), methylene blue (b), and their adsorption capacity (q_e) by both PES-NH₂ with AC-COOH using the in situ and ex situ techniques in comparison with the control (PES-NH₂) (c) at pH = 2 for acid red and pH = 9 for methylene blue.

Table 3. The percentage adsorption of acid red (A.R) by PES-NH₂ with different concentrations of AC-COOH using the in situ and ex situ techniques; $V = 10$ mL, acid red conc. = 20 ppm, polymer wt. = 10 mg, $\lambda = 530$ nm, $t = 20$ °C, and pH = 2.

Polymers	%Adsorption of A.R	q_e (mg dye/g adsorbent)
Control (PES-NH ₂)	21.749	4.3498
PES-NH ₂ with 2% AC-COOH in situ	42.60	4.9202
PES-NH ₂ with 5% AC-COOH in situ	35.538	7.1076
PES-NH ₂ with 10% AC-COOH in situ	37.332	7.4664
PES-NH ₂ with 20% AC-COOH in situ	60.969	12.194
PES-NH ₂ with 2% AC-COOH ex situ	26.457	5.2915
PES-NH ₂ with 5% AC-COOH ex situ	36.996	7.3991
PES-NH ₂ with 10% AC-COOH ex situ	40.471	8.0942
PES-NH ₂ with 20% AC-COOH ex situ	61.323	12.265

Table 4. The percentage adsorption of methylene blue (M.B) by PES-NH₂ with different concentrations of AC-COOH using the in situ and ex situ techniques; $V = 10$ mL, acid red conc. = 20 ppm, polymer wt. = 10 mg, $\lambda = 530$ nm, $t = 20$ °C, and pH = 9.

Polymers	%Adsorption of M.B	q_e (mg dye/g adsorbent)
Control (PES-NH ₂)	33.861	1.6931
PES-NH ₂ with 20% AC-COOH in situ	68.453	3.4227
PES-NH ₂ with 20% AC-COOH ex situ	88.063	4.4032

Overall, both PES-NH₂ with AC-COOH in situ and ex situ showed excellent adsorption rates with both the acid red (anionic) and methylene blue (cationic) dyes in comparison with the control as shown in Table 3 and 4, respectively. However, because acid red (20 ppm) showed a good adsorption capacity (q_e) up to 12 (Figure 7c) in comparison with methylene blue (5 ppm) which gave q_e between 3 and 4 for PES-NH₂ with AC-COOH in situ and ex situ (Figure 7c), the effect of different impact factors (including pH, temperature, time, and mass) was further examined on the adsorption of acid red dye by PES-NH₂ in situ and ex situ with AC-COOH.

3.3. Retention Outline of Acid Red from the Aqueous Solution onto Solid Phases PES-NH₂ with In Situ and Ex Situ AC-COOH

The adsorption of acid red dye in an aqueous medium with different pH values using PES-NH₂ in situ and ex situ with AC-COOH solid phase were investigated at r.t and after 1 h of shaking. At equilibrium, the acid red quantity in the aqueous medium was photometrically measured [11]. It was observed when the % E was measured for the acid red adsorption onto the AC-COOH in situ and ex situ, there was a remarkable reduction in % E as the pH values increased as shown in Figure 8a. Therefore, from this pH study, it was found that the pH values in the range of 1–2 were the best pH conditions to adsorb the acid red dye from the aqueous medium. The pH value of 1.5, which was obtained using HCl, was chosen for this current work.

The second impact factor was the contact time of the red acid analyte and PES-NH₂ with AC-COOH solid phase adsorbent. Figure 8b shows the investigation study of the effect of the contact time for acid red dye adsorption by PES-NH₂ with AC-COOH in situ and ex situ. In this figure, there was an increase in the adsorption process when the contact time was increased. After 40 min of contact time, most of the acid red dye was adsorbed into the polymer solid phase. However, when the contact time was prolonged, an equilibrium of the percentage of adsorption (in 120 min) was observed. As shown in Figure 8b, it can be clearly seen that there were two consecutive steps needed for the adsorption of acid red on PES-NH₂ with 20% of AC-COOH, in situ and ex situ. The first step was the fastest, in which the acid red transferred from the solution to the PES-NH₂ with a surface of 20% AC-COOH in situ and ex situ whereas the second one was the slowest in which the acid red dye was diffused in the PES-NH₂ with bundles of 20% AC-COOH in situ and ex situ.

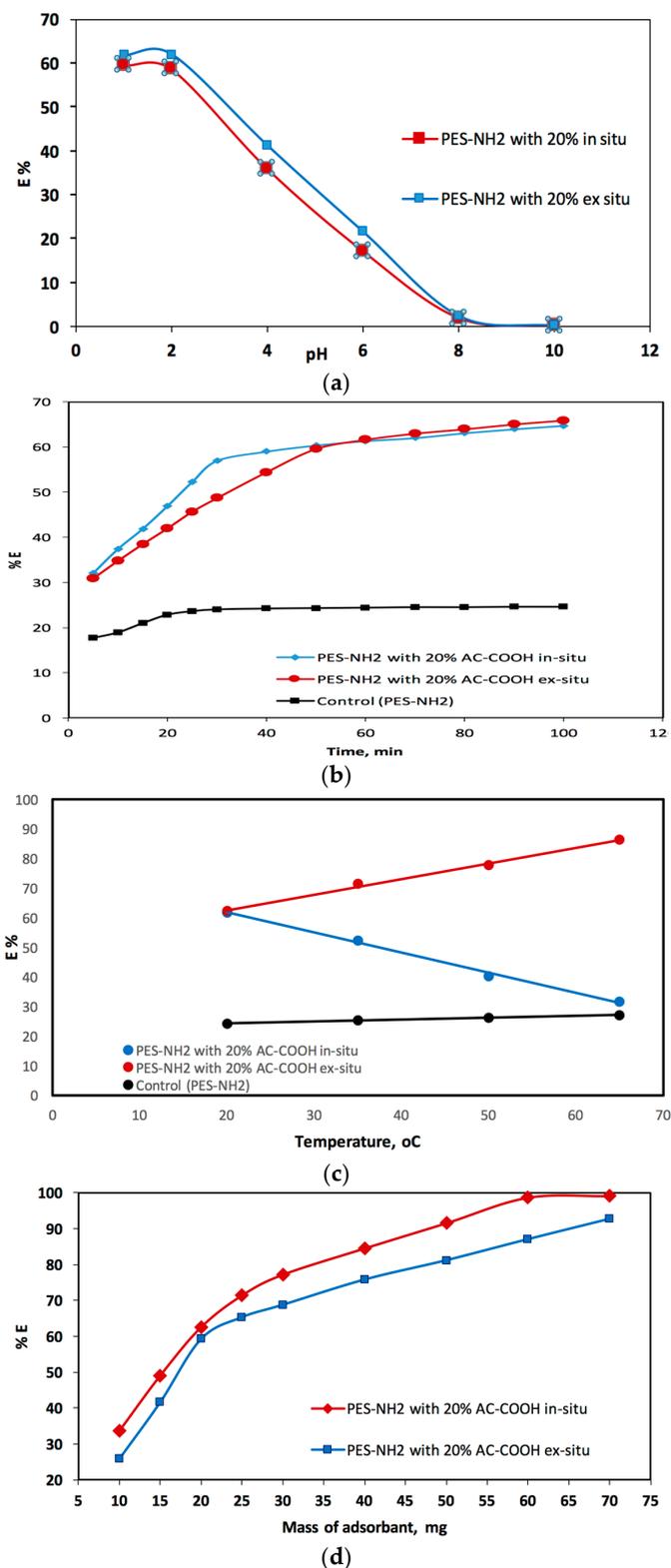


Figure 8. The effect of the solution pH with a duration of 1 h of shaking (a), the shaking time at pH = 1–2 (b), the temperature at 20 °C, 35 °C, 50 °C, and 60 °C (c), and the masses of the polymer (mg) with a pH at 1–2 and a 1 h shaking time at 20 ± 0.1 °C on the adsorption percentage of acid red (20 ppm) from aqueous solutions onto the PES–NH₂ in situ with AC–COOH (in red color) and the PES–NH₂ ex situ with 20% AC–COOH (20 mg) (in blue color) with a shaking time of 1 h at 20 ± 0.1 °C (d).

In addition to the pH and contact time factors, the third impact factor that affected the adsorption mechanism was the temperature for the sample solutions. The impact of 20 °C, 35 °C, 50 °C, and 65 °C temperatures were chosen in this work in order to investigate the impact of these temperatures on the adsorption of acid red dye by the polymer solid phase. As shown in Figure 8c, there was a remarkable increase in %adsorption for the acid red dye by PES-NH₂ with the 20% AC-COOH in situ and ex situ solid phase. However, PES-NH₂ with 20% AC-COOH in situ showed a reversed performance; meaning, as the solution temperature increased, the percentage of acid red adsorption decreased. The results for this adsorption process in Figure 8c clearly showed the different thermodynamic behavior of PES-NH₂ with 20% AC-COOH in situ, which showed an endothermic nature in comparison with PES-NH₂ with 20% AC-COOH ex situ, which showed an exothermic nature similar to the control (PES-NH₂).

Lastly, the effect of the mass on %adsorption for the acid red adsorbed from the liquid medium was examined with an acid red concentration of 20 mg/L (Figure 8d). Figure 8d shows that the %adsorption for the acid red dye that was adsorbed from the liquid medium raised as the PES-NH₂ with 20% AC-COOH in situ and ex situ doses increased. This increase in the percentage is because of increasing number of activated carbon sites in the PES-NH₂ surface/matrix for adsorbing the acid red dye from the aqueous medium. The VIS spectrum of the acid red recorded in the aqueous medium exhibited an absorption peak at 530 ± 2 nm as shown in Figure 9. However, this peak decreased dramatically after shaking with PES-NH₂ with 20% AC-COOH (Figure 9), and this behavior confirms the efficiency of PES-NH₂ in situ and ex situ with 20% AC-COOH for the acid red dye adsorption from the liquid medium.

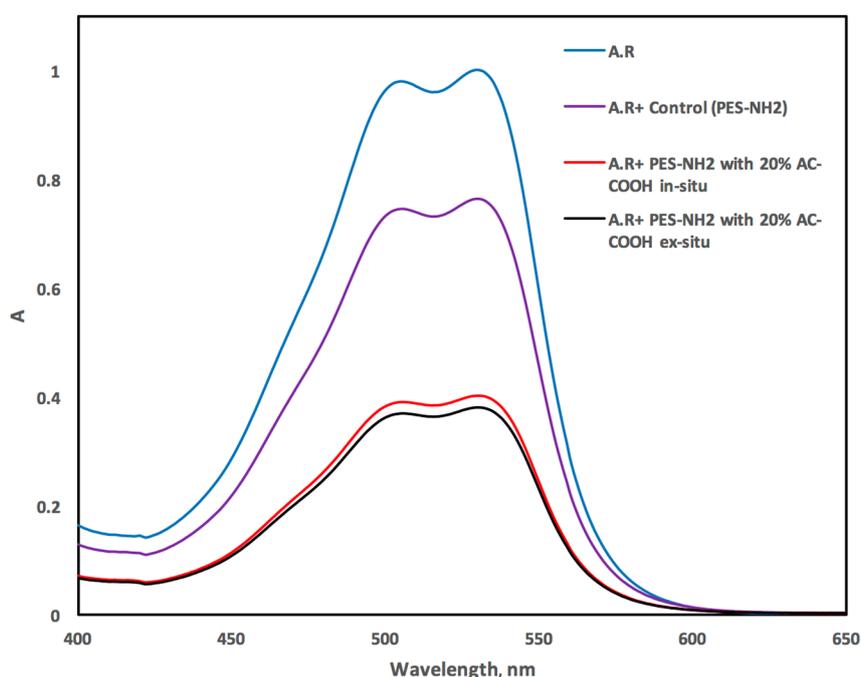


Figure 9. The visible spectra of 20 ppm concentration of acid red in the aqueous phase (blue line), after shaking with 20 mg of the control (PES-NH₂) (purple line), after shaking with 20 mg of PES-NH₂ in situ with 20% AC-COOH (red line), and after shaking with 20 mg of PES-NH₂ ex situ with 20% AC-COOH (black line).

3.4. The Adsorption Kinetic Performance for the Acid Red Dye by PES-NH₂ with In Situ and Ex Situ 20% AC-COOH

The adsorption kinetics of acid red from aqueous solutions by PES-NH₂ with the AC-COOH solid phase is necessary to deeply understand the adsorption reactions and the adsorption mechanisms.

The intraparticle dispersal and film dispersal are two important factors that the retention of acid red adsorption on PES-NH₂ with the AC-COOH solid phase relies on, and the faster the factor is, the likelier it will be the one that will govern the overall transport percentage.

The acid red adsorbed process half-life time ($t_{1/2}$) by PES-NH₂ with the AC-COOH solid phase from the aquatic medium was determined by plotting $\log C/C_0$ versus time as shown in Figure 10a, in which C and C_0 are the red acid dye initial quantity before and after it was adsorbed, respectively. The value of $t_{1/2}$ was found to be 1.71 ± 0.07 min for PES-NH₂ in situ with 20% AC-COOH and 1.83 ± 0.06 for PES-NH₂ ex situ with 20% AC-COOH and 1.46 ± 0.04 for the control (PES-NH₂). This came in agreement with the values of $t_{1/2}$ reported recently [17]. Consequently, the kinetics of acid red adsorption onto PES-NH₂ with AC-COOH adsorbent relies on both the intraparticle dispersal and film dispersal, in which the faster the factor is, the likelier it will be that the factor will govern the overall transport percentage.

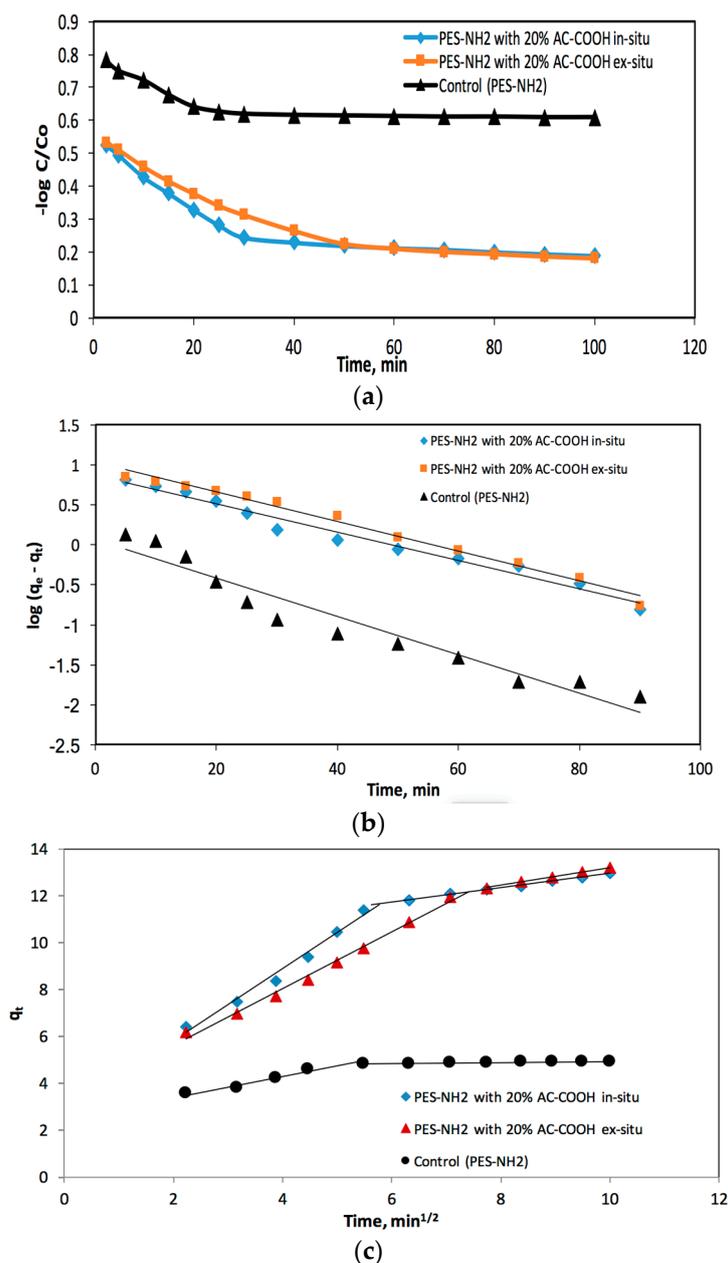


Figure 10. Cont.

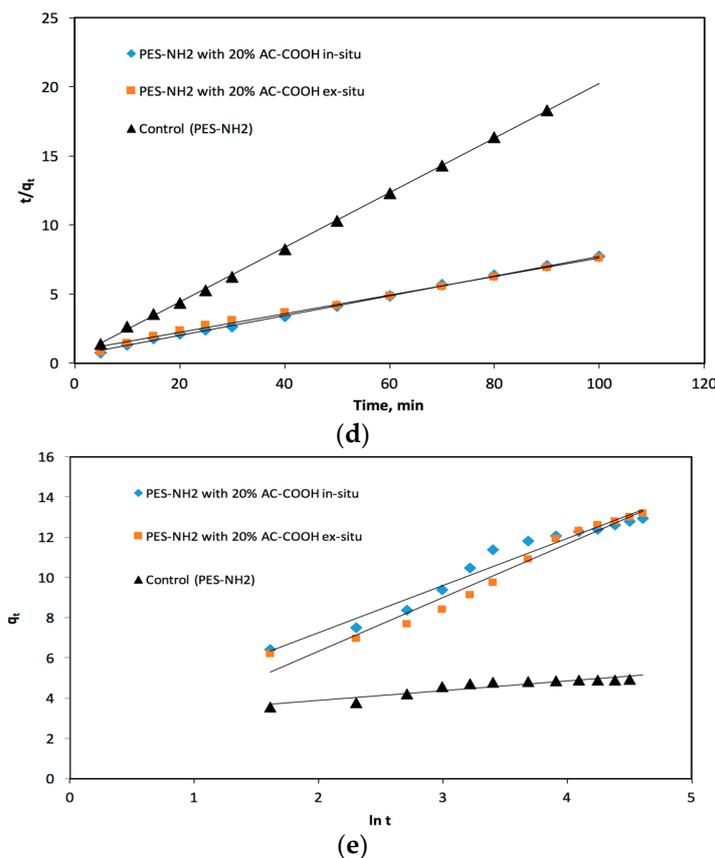


Figure 10. The plot of $\log C/C_0$ of the acid red sorption from an aqueous media onto PES-NH₂ in situ with 20% AC-COOH, PES-NH₂ ex situ with 20% AC-COOH, and the control (PES-NH₂) versus time (a), Weber–Morris plot of the sorbed acid red onto PES-NH₂ in situ with 20% AC-COOH, PES-NH₂ ex situ with 20% AC-COOH, and the control (PES-NH₂) versus the square root of time (b), the Lagergren plot of the sorbed acid red onto PES-NH₂ in situ with 20% AC-COOH, PES-NH₂ ex situ with 20% AC-COOH, and the control (PES-NH₂) versus time at 20 °C (c), pseudo-second-order plot of acid red uptake onto PES-NH₂ with 20% AC-COOH in situ, PES-NH₂ with 20% AC-COOH ex situ, and the control (PES-NH₂) versus time at 20 °C (d), and the Elovich model plot for acid red uptake onto PES-NH₂ in situ with 20% AC-COOH, PES-NH₂ ex situ with 20% AC-COOH, and the control (PES-NH₂) (q_t) against ($\ln t$) at 20 °C (e).

The adsorption of acid red species on the PES-NH₂-AC-COOH solid phase was tested with a model developed by Weber and Morris [18]:

$$q_t = R_d (t)^{1/2} \quad (1)$$

q_t is the acid red adsorption concentration in respect to time (t), and R_d refers to intra-particle transport rate values. The q_t versus time plot was presented in Figure 10b. The values of R_d were calculated from the two distinct slopes of the Weber–Morris plots (Figure 10b). For PES-NH₂ in situ with 20% AC-COOH, the values were found to be about 1.536 and 0.307 mg/g while, for PES-NH₂ ex situ with 20% AC-COOH, the values were found to be about 1.207 and 0.421 mg/g, but for the control (PES-NH₂), the values were found to be about 0.424 and 0.025 mg/g, respectively.

The Lagergren equation is a well-known equation which defines the adsorption rate for aqueous phase systems. The variation of the acid red dye adsorption from liquid solutions onto PES-NH₂ with AC-COOH was also tested with a Lagergren equation [19]:

$$\log(q_e - q_t) = \log q_e - K_{\text{lager}} \cdot t / 2.303 \quad (2)$$

The q_e stands for the acid red dye quantity that was adsorbed at equilibrium per sorbent mass, whereas K_{Lager} stands for the first order total rate values for the retention mechanism, and t indicates the time. The $\log(q_e - q_t)$ versus the time plot in Figure 10c was not a straight line and the calculated value of K_{Lager} and q_e were found to be about 0.041 min^{-1} and 7.43 mg/g for PES-NH₂ with 20% AC-COOH in situ, respectively, with a correlation coefficient of $R^2 = 0.978$, while the values for PES-NH₂ with 20% AC-COOH ex situ were found to equal 0.043 min^{-1} and 10.68 mg/g , respectively, with a correlation coefficient of $R^2 = 0.987$. For the control (PES-NH₂), the values were about 0.055 min^{-1} and 1.16 mg/g , respectively, with a correlation coefficient of $R^2 = 0.937$. All this data and the comparison between the calculated value of q_e with that measured experimentally ($q_{e, \text{exp}}$) confirmed that the first order kinetic model is not a suitable model to describe the adsorption of acid red species onto the used PES-NH₂ with AC-COOH sorbent.

The pseudo-second-order model has been investigated as a Langmuir kinetics type [19], taking into consideration two factors: the first is that the analyte concentration with respect to time is a constant and the second factor is that the binding sites rely on the analyte adsorbed quantity at equilibrium. The pseudo-second-order linear equation was stated as follows:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \quad (3)$$

where h is equal to $k_2q_e^2$ which refers to the initial adsorption level, whereas q_e and q_t are the quantity of adsorbed analyte per mass unit at any selected time at equilibrium. Under these conditions, the $\frac{t}{q_t}$ versus the time (t) plot was applied as shown in Figure 10d, in which it was shown as linear. Then, from the slope and intercept, the second order constant (k_2) and equilibrium capacity (q_e) were obtained first for PES-NH₂ with 20% AC-COOH in situ and they were found to equal $8.84 \times 10^{-3} \text{ g} \cdot (\text{mg} \cdot \text{min})^{-1}$ and 13.95 mg/g , respectively, with an excellent correlation ($R^2 = 0.999$), while for PES-NH₂ with 20% AC-COOH ex situ, they were found to be equal to $5.3 \times 10^{-3} \text{ g} \cdot (\text{mg} \cdot \text{min})^{-1}$ and 14.79 mg/g , respectively, with an excellent correlation ($R^2 = 0.995$). For the control (PES-NH₂), the k_2 and q_e values were found to be equal to $8.8 \times 10^{-2} \text{ g} \cdot (\text{mg} \cdot \text{min})^{-1}$ and 5.05 mg/g , respectively, with a superb correlation ($R^2 = 0.999$). It is clearly seen from these reported data that all the experimental measured values were considered suitable values. The pseudo-second-order rate constant (k_2) values rely on different experimental factors including the initial PES-NH₂-AC-COOH concentration, the pH values, as well as the temperature [19].

The adsorption capacity rate is usually determined using the Elovich equation [19]. This equation is appropriate mostly for systems that show kinetics of chemisorptions and it can be also applied to a system in which the adsorbent surface area is heterogeneous. This equation can be calculated as follows:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \quad (4)$$

The α value ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) stands for the original adsorption rate value whereas the β value ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) stands for the coefficient of desorption. The q_t against the $\ln t$ plot was applied as shown in Figure 10e and the relationship between them was linear. The Elovich factors (the α as well as β values) were calculated from the intercepts and the slopes obtained from Figure 10e. These values for the acid red dye were found to be about $1.12 \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ and $2.345 \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$, respectively, adsorbed onto PES-NH₂ with 20% AC-COOH in situ, and they were found to be about $0.542 \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ and $2.671 \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$, respectively, adsorbed onto PES-NH₂ with 20% AC-COOH ex situ. Meanwhile, the α , β values were found to equal $712.8 \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ and $0.493 \text{ mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$, respectively adsorbed onto the control (PES-NH₂).

The above experimental data measured from different kinetic models (including the pseudo-first-order kinetic (Lagergren), the pseudo-second-order kinetic, as well as the Elovich kinetic) were applied and used in order to determine the kinetic behaviors of the acid red dye adsorption. From the comparisons between the experimental and calculated values of q_e as well as the values of the correlation coefficients that were all determined from these three models as summarized in Table 5, it can be seen

that the most suitable model for the kinetic behavior of the acid red dye that was adsorbed on PES-NH₂ with the AC-COOH solid phase was the pseudo-second-order kinetic model.

Table 5. The different kinetic models' parameters for the adsorption of acid red on PES-NH₂ in situ with 20% AC-COOH, PES-NH₂ ex situ with 20% AC-COOH, and the control (PES-NH₂) at 293 K.

The pseudo-first-order kinetic (Lagregen) model	$q_{e, \text{exp}}$ (mg/g)	$q_{e, \text{calc}}$ (mg/g)	$k_1, \text{g} \cdot (\text{mg} \cdot \text{min})^{-1}$	R^2
PES-NH ₂ (Control)	4.92	1.16	0.055	0.937
Control in situ with 20% ACOOH	12.94	7.43	0.041	0.978
Control ex situ with 20% ACOOH	13.18	10.68	0.043	0.987
The pseudo-second-order kinetic model	$q_{e, \text{exp}}$ (mg/g)	$q_{e, \text{calc}}$ (mg/g)	$k_2, \text{g} \cdot (\text{mg} \cdot \text{min})^{-1}$	R^2
PES-NH ₂ (Control)	4.92	5.05	8.8×10^{-2}	0.999
Control in situ with 20% ACOOH	12.94	13.95	8.84×10^{-3}	0.999
Control ex situ with 20% ACOOH	13.18	14.79	5.3×10^{-3}	0.995
Elovich kinetic model	$\alpha, \text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$	$\beta, \text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$	-	R^2
PES-NH ₂ (Control)	712.8	0.493	-	0.871
Control in situ with 20% ACOOH	1.12	2.345	-	0.962
Control ex situ with 20% ACOOH	0.542	2.671	-	0.97

3.5. Thermodynamic Characteristics of Acid Red Retention onto the Solid Phase

The adsorption of acid red onto PES-NH₂ with the AC-COOH solid phase was investigated with various temperatures between 293 K and 338 K in order to find the acid red retention values of these polymers. The thermodynamic factors including ΔH , ΔS , and ΔG were determined by utilizing the below equations [20]:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

$$\Delta G = -RT \ln K_c \quad (7)$$

The ΔH stands for enthalpy, ΔS refers to the entropy, and ΔG defines the Gibbs free energy variations. T refers to the temperature in the Kelvin system, whereas the gas constant is abbreviated as R ($\approx 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). The equilibrium constant (K_c) relies on the adsorption mechanism for the fractional attainment which is abbreviated as Fe. The K_c values were calculated in order to determine the acid red dye retention on the PES-NH₂ with the AC-COOH solid sorbent at equilibrium the below equation:

$$K_c = \frac{q_e}{1 - q_e} \quad (8)$$

The $\ln K_c$ versus $1000/T$ plot was applied for the retention of acid red dye onto the solid phase of PES-NH₂ with AC-COOH, in which the relationship was found to be linear as shown in Figure 11 with various temperatures between 293 and 338 K. From Figure 11, it can be seen that both the control (PES-NH₂) and the PES-NH₂ with 20% AC-COOH ex situ equilibrium constants increased when the temperature increased, which suggest that that the acid red dye retention on the solid phase sorbents is an endothermic mechanism. However, the PES-NH₂ with 20% AC-COOH using the in situ technique equilibrium constant decreased when the temperature increased which suggests that the acid red dye retention on the solid phase sorbents (PES-NH₂ in situ with 20% AC-COOH) is an exothermic mechanism. The ΔH , ΔS , and ΔG values that were determined for acid red retention were determined from the $\ln K_c$ versus $1000/T$ plot utilizing the slopes and intercepts as shown in Figure 11. The ΔH , ΔS , and ΔG values for control (PES-NH₂) were found to be around $2.78 \pm 0.1 \text{ kJ} \cdot \text{mol}^{-1}$, $0.0025 \pm 0.00003 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, and $277 \pm 0.02 \text{ kJ} \cdot \text{mol}^{-1}$ (at 293 K), respectively, whereas for PES-NH₂ ex situ with 20% AC-COOH,

they were found to be equal to $24.04 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$, $85.79 \pm 0.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and $-1.1 \pm 0.06 \text{ kJ}\cdot\text{mol}^{-1}$ (at 293 K), respectively. However, the values for PES-NH₂ with 20% AC-COOH in situ were found to be $-23.16 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$, $-74.85 \pm 0.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and $-1.23 \pm 0.08 \text{ kJ}\cdot\text{mol}^{-1}$ (at 293 K), correspondingly. The value of ΔH for the control (PES-NH₂) and PES-NH₂ ex situ with 20% AC-COOH reveals that the uptake mechanism was endothermic, which exhibits the bond energy variations between the adsorbent solid phase and the analyte. However, the value of ΔH for PES-NH₂ in situ with 20% AC-COOH reveals that the uptake mechanism was exothermic.

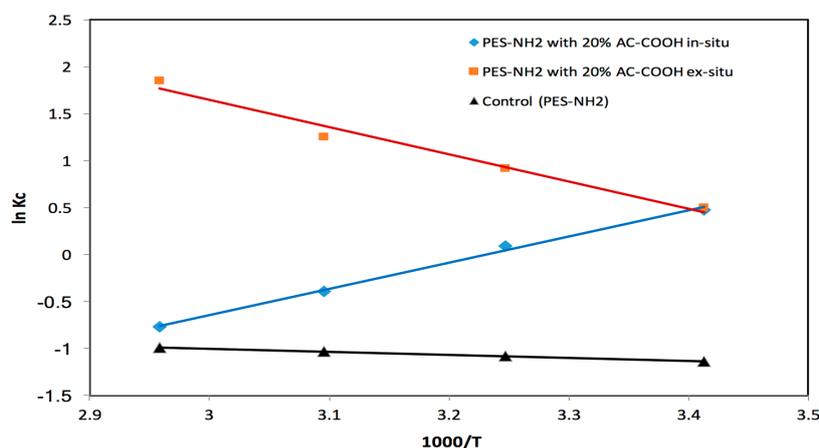


Figure 11. The plot of $\ln K_c$ of acid red sorption from an aqueous media onto PES-NH₂ in situ with 20% AC-COOH, PES-NH₂ ex situ with 20% AC-COOH, and the control solid phase particles versus $1000/T$.

The ΔS positive values indicate there is an increase in the freedom degree at the solid-liquid system during the acid red binding, and this is because of the presence of water molecules that are released by hydration spheres occurred during the adsorption mechanism. On the other hand, the ΔS negative values indicate that the entropy (reorientation phase) is governed at the activation state and nonelectrostatics interactions between the analyte (acid red dye) and the adsorbed material (PES-NH₂-AC-COOH). In addition, the ΔG negative values at a temperature of 293 K for both PES-NH₂ with in situ 20% AC-COOH and PES-NH₂ ex situ with 20% AC-COOH indicate that the interactions that form during the adsorption of acid red retention on PES-NH₂ with AC-COOH solid phase were spontaneous. In contrast, the positive value of ΔG at 293 K for the control (PES-NH₂) indicates that interactions that form during the adsorption of acid red retention on PES-NH₂ solid phase were nonspontaneous.

3.6. Environmental Applications

In order to investigate the efficiency of the PES-NH₂-AC-COOH solid phase use in environmental applications, this study used tap water and seawater samples to explore the capability of this polymer in removing red acid dye from these samples. The tap water was obtained from our chemistry tap at King Abdul-Aziz University while the seawater was obtained from the Red Sea at the Jeddah coast in Saudi Arabia, and a deionized water sample was also used as a third sample. For the seawater and tap water samples, the acid red concentrations were below the U.V. detection. Hence, these samples were spiked with acid red dye (20 mg/L) and PES-NH₂ ex situ with 20% AC-COOH (70 mg) and PES-NH₂ in situ with 20% AC-COOH (80 mg). Under the optimized conditions including a pH of 1, a temperature of 293 K, and a 1 h of shaking time, the percentages of red acid adsorbed from the Red Sea water samples were found to be 92.68% and 91.91% for PES-NH₂ ex situ with 20% AC-COOH and PES-NH₂ in situ with 20% AC-COOH, respectively. The percentages of acid adsorbed from the tap water samples were found to be 96.34% and 95.94% for PES-NH₂ ex situ with 20% AC-COOH and PES-NH₂ in situ with 20% AC-COOH, respectively, as shown in Figure 12.

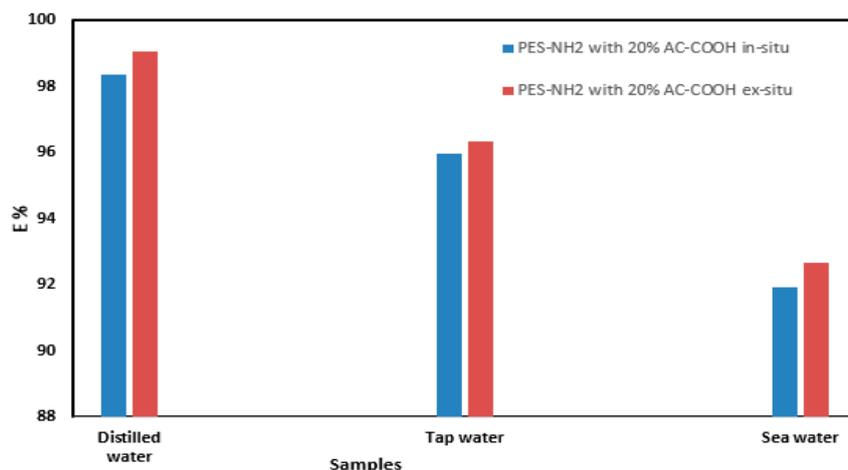


Figure 12. The adsorption percentages of acid red from different real samples by PES-NH₂ with 20% AC-COOH (experimental conditions: 20 mL solution, pH 1.5, 60 min, 293 K, acid red concentration 20 mg·L⁻¹, 70 mg in the case of PES-NH₂ ex situ with 20% AC-COOH, and 80 mg in the case of PES-NH₂ in situ with 20% AC-COOH).

In order to test the reusability of the fabricated polymers, the used samples of PES-NH₂ with 20% AC-COOH by both ex situ and in situ techniques were cleaned afterward by washing these samples with acetone and left to be dried. Then, the PES-NH₂ ex situ and in situ with 20% AC-COOH samples were reused again. The acid red dye was re-adsorbed again (three cycles) with approximately the same adsorption percentage rates as the first time. Therefore, PES-NH₂ with 20% AC-COOH is an efficient method to be reused for more than one cycle as the acid red dye is adsorbed from the aquatic environment without any reduction in its adsorption capability.

4. Conclusions

In this current study, PES was chemically modified to PES-NH₂ following a two-step reaction: a nitration reaction followed by a reduction reaction. The chemical modification of PES was introduced in order to overcome the hydrophobicity of this polymer. According to the FT-IR, XRD, and thermal analyses results, when PES-NH₂ was in situ with AC-COOH, there was a difference in the chemical structures of these polymers in comparison with the control, suggesting strong noncovalent interactions between the PES-NH₂ and AC-COOH. Contrary to the in situ technique, the ex situ method of the polymer with AC-COOH exhibits a slight change in the chemical structures in comparison to the control. In addition, the dye adsorption results showed excellent adsorption rates of acid dye 1 and methylene blue dyes as the concentrations of AC-COOH increased in both in situ and ex situ techniques with PES-NH₂. The results also showed the optimized conditions were fundamental factors for maximizing the acid red dye adsorption rate and they were found to be at a pH of 1.5, for a duration of 1 h, and at a temperature of 293 K. Additionally, the mass of the PES-NH₂-AC-COOH is a very important factor as the more mass used, the higher the obtained dye adsorption rate. After going through different kinetic models (including the pseudo-first-order kinetic (Lagergren), the pseudo-second-order kinetic, as well as the Elovich kinetic model) to determine the adsorption behavior of the acid red dye, this study's results showed that the pseudo-second-order kinetic model was the most appropriate model for the kinetic behavior of the acid red dye adsorption by PES-NH₂-AC-COOH.

Author Contributions: N.A.A. carried out the experimental work, collected the data and wrote the manuscript. M.A.H. and K.A.A. designed the research work, explained the results and revised the manuscript. A.M.A. explained the results and revised the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

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