

Article

Amine-Grafted Pomegranate Peels for the Simultaneous Removal of Nitrate and Phosphate Anions from Wastewater

Wafae Abbach ^{1,2}, Charaf Laghlimi ^{1,2}  and Jalal Isaad ^{1,2,*} 

¹ Department of Chemistry, Faculty of Science and Technology of Al-Hoceima, BP 34., Ajdir, Al-Hoceima 32003, Morocco

² ERCI2A, FSTH, Abdelmalek Essaadi University, Tetouan 93000, Morocco

* Correspondence: j.isaad@uae.ac.ma; Tel.: +212-5398-07172

Abstract: Pomegranate peel (PP), a by-product of agro-food consumption, has a low adsorption capacity for nitrate and phosphate ions in aqueous media, but its surface is very rich in alcohol functional groups. In this work, the surface of pomegranate peels was functionalized by chemo-grafting 3-(2-Aminoethylamino) propyl] trimethoxy silane (AEAPTES) using the availability of alcohol groups to increase the adsorption capacity of the resulting adsorbent (PP/AEAPTES) towards nitrate and phosphate ions. The prepared PP/AEAPTES adsorbent was analyzed by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Zeta potential, and X-ray photoelectron spectrometry (XPS). Under experimental conditions, the adsorption capacity of PP/AEAPTES has been found to be 124.57 mg/g and 94.65 mg/g for NO_3^- and PO_4^{3-} , respectively, at pH 6 over a wide temperature range, and adsorption is exothermic for NO_3^- and endothermic for PO_4^{3-} , as well as spontaneous and physical in nature. The adsorptions of NO_3^- and PO_4^{3-} were also correctly described by the Langmuir isotherm and followed the pseudo-second-order model. The ability of PP/AEAPTES to adsorb NO_3^- and PO_4^{3-} ions under real conditions was evaluated, and efficient regeneration and repetitive use of PP/AEAPTES was successfully achieved up to 5 cycles.

Keywords: water; nitrate; phosphate; removal; AEAPTES; pomegranate peels



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1. Introduction

Both nitrate (NO_3^-) and phosphate (PO_4^{3-}) anions are potentially toxic at high concentrations. In a biological environment, NO_3^- is converted to NO_2^- ions by bacteria in the digestive system (specifically the mouth and stomach), and NO_2^- is able to react with blood hemoglobin to generate methemoglobin, which in turn causes hypoxia [1]. High levels of nitrate in drinking water could also have a harmful impact on the health of humans, particularly for infants and the elderly. Several studies have shown an association between long-term exposure to high levels of nitrates and nitrites, notably through the consumption of processed meats, and the development of cancer of the colorectal gland [2]. On the other hand, PO_4^{3-} anions can cause excessive growth of algae and aquatic plants when present in high concentrations in freshwater water sources. This can lead to eutrophication, which reduces oxygen levels in the water and harms fish and other aquatic life [3,4].

Considering the serious health concerns due to the excessive concentrations of NO_3^- and PO_4^{3-} in potable water, the limit levels for NO_3^- and PO_4^{3-} ions in potable water are limited to 40 mg/L and 0.1 mg/L, respectively, according to the WHO [5]. Therefore, it is important to properly reduce the levels of NO_3^- and PO_4^{3-} in waters and develop methods to remove these anions in order to comply with applicable regulations.

In this regard, a number of innovative processes to remove NO_3^- and PO_4^{3-} from wastewater were developed, involving biological, chemical, and physical treatment methods. Biological processes are used to remove NO_3^- and PO_4^{3-} , including biological denitrification and/or dephosphating bacteria [6–9], which are able to convert NO_3^- and

PO_4^{3-} anions into less harmful forms such as nitrogen gas and phosphoric acid, respectively. These methods are commonly employed in wastewater treatment stations and are known as denitrification and biological phosphorus removal. However, biological denitrification and phosphate removal are lengthy processes that often need carbon sources and proper biological sludge disposal. Chemical methods to remove NO_3^- and PO_4^{3-} are based on the reaction between a number of iron and aluminum salts with NO_3^- and PO_4^{3-} to form insoluble precipitates that are easily removed from water [10–14]. Other chemical techniques to remove NO_3^- are involved in the chemical reduction of NO_3^- by chemical reductants, especially hydrazine [15], sodium sulfite [16–18], zero-valent metal [19–23], and hydrogen [24,25]. Physical technologies have also been used, such as the adsorption of NO_3^- and PO_4^{3-} onto activated polymers [26–28], biochars [29–32], mineral adsorbent materials [33–35], and organic-inorganic hybrid bio-composites [36–40]. It is important to note that these biological, chemical, and physical methods mentioned above have many limitations in use. They require the use and/or generation of toxic chemicals that can cause other environmental and health problems, as well as their high economic costs and low capacity to remove NO_3^- and PO_4^{3-} ions.

In order to surmount these limitations, the use of agro-resources as a potential environmental and economic management tool remains a very promising alternative to synthetic adsorbents because they are naturally available, less expensive, environmentally friendly, and biodegradable. In fact, in general, agro-resources are increasingly used in water treatment to reduce the environmental impact of many activities, such as fabric dyeing [41–44], molecular detection of chemical elements [45,46], and pollutant removal. In this regard, several studies have reported the use of agro-wastes (raw and modified) as adsorbents for several pollutants such as dyes [47,48], heavy metals [49–51], and $\text{NO}_3^-/\text{PO}_4^{3-}$ anions [52–56].

The natural raw materials mentioned above adsorb pollutants but inefficiently with low adsorption capacity (q_e). Therefore, chemical activation of the surface is needed to improve the adsorption efficiency of agricultural waste [53–56] in order to remove the pollutants concerned. Several chemical activation agents have been used to chemically activate the surface of agricultural waste, such as dimethylamine/epichlorohydrin grafted onto the surface of several by-products (sugarcane bagasse, hazelnuts, and rice shells). This chemical activation improved the ability of these by-products to adsorb NO_3^- which expected q_e of 55.6 mg/g in the case of rice peel [54–56]. Other chemicals with amino functions, such as cetyltrimethylammonium bromide [53], polyethyleneimine [57], N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHMAC) [55], and 3-aminopropyltriethoxy silane (APTES) [58] have also been commonly used to improve the adsorption of NO_3^- anions. Many studies in the last few years have focused on developing new hybrid materials and composites based on agricultural wastes and amino-alkyl silane (AAS) derivatives for the effective removal of various pollutants [58–64]. This is due to the presence of the amine function of the amino-alkyl silane derivative, which proves the great interest in the chemical surface functionalization of the adsorbents by the AAS moiety. Considering this context, it is essential to develop a novel AAS/agro-waste for effective application in NO_3^- and PO_4^{3-} ions removal.

Hence, we propose in this work a novel adsorbent to remove NO_3^- and PO_4^{3-} from contaminated aqueous solution. The novel adsorbent PP/AEAPTES (Figure 1) was prepared by surface functionalization of pomegranate peels (PP) with [3-(2-Aminoethylamino) propyl] trimethoxy silane (AEAPTES) as an amino-alkyl silane derivative, through a chemical grafting between the silane group of AEAPTES and the hydroxy groups (-OH) available on the surface of PP. Pomegranate peel was selected for amine grafting over other biomasses due to the availability of pomegranate in Morocco. On the other hand, pomegranate produces a lot of peels as waste available as raw material that can be valorized by producing efficient adsorbents by amine grafting on the surface of PP. The use of amino-alkyl silanes to functionalize the surface of inorganic substrates, including silica and its derivatives, has been widely studied in the literature [61–64]. However, there is little work reporting the

functionalization of the agro-waste surface by AEAPTES. The main objectives of grafting AEAPTES onto the surface of pomegranate peel consist in improving the performance of the new adsorbent PP/AEAPTES, compared to the raw pomegranate peels, in removing nitrate and phosphate ions due to the interactions that can occur between NO_3^- and PO_4^{3-} and the $-\text{NH}_2$ groups available on the PP/AEAPTES surface.

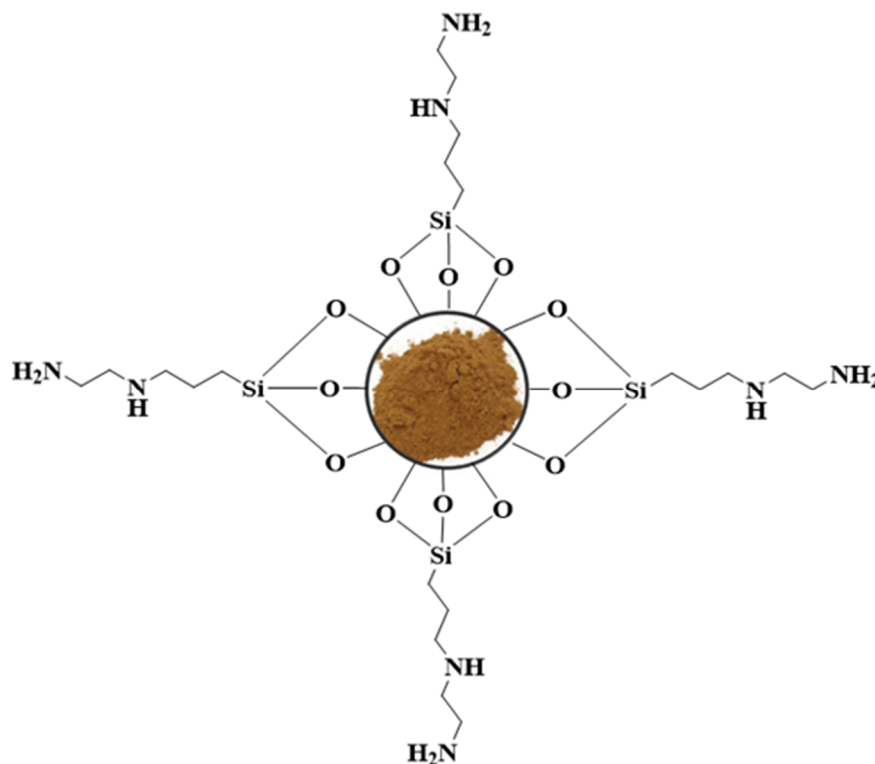


Figure 1. Structure of the adsorbent PP/AEAPTES.

The novel adsorbent PP/AEATES was fully characterized using physical and chemical methods, including FT-IR, XRD, XPS, and zero charge point. In addition, the behavior of PP/AEAPTES towards NO_3^- and PO_4^{3-} anions was studied according to the pH of the solution, contact time, adsorbent dose, initial concentration, and temperature.

2. Materials and Methods

All the chemical compounds are of reagent quality (Aldrich Chemical) and were used without purification. The pomegranates used in this study are of the “Safri” variety collected from the Ouled Abdellah region (Fqih Ben Salah province—Morocco). All the experimental procedures and characterization methods used in his work are described in the supporting materials. All statistical calculations were performed using OriginPro® 2023b graphing and data analysis software.

2.1. Preparation and Functionalization of Modified Pomegranate Peels

The preparation of PP/AEAPTES is summarized in Figure 2. First, the pomegranate peels were collected and air-dried for 6 days, and then the obtained pomegranate peels were mechanically ground to obtain PPB powder 1. In order to remove dust, soluble impurities, coloring matters, and water-soluble tannins, the PPB powder 1 was washed with an acidic solution (HCl, 1 M) and with distilled water and then boiled for one hour at 90 °C several times until the supernatant was colorless. The obtained residue was dried at 100 °C to a constant weight to obtain PPB powder 2. The chemical fixation of AEAPTES was carried out by mixing AEAPTES and PPB powder 2 with a ratio of (4:1 *w/w*) in a mixture of EtOH/deionized water (4/1.5 *v/v*) at a temperature of 90 °C for 6 h [63]. The resulting

material (PP/AEAPTES) was recovered through filtration on filter paper, washed 5 times with a solution of EtOH/deionized water (1/1 *v/v*), and dried for several hours at 65 °C.

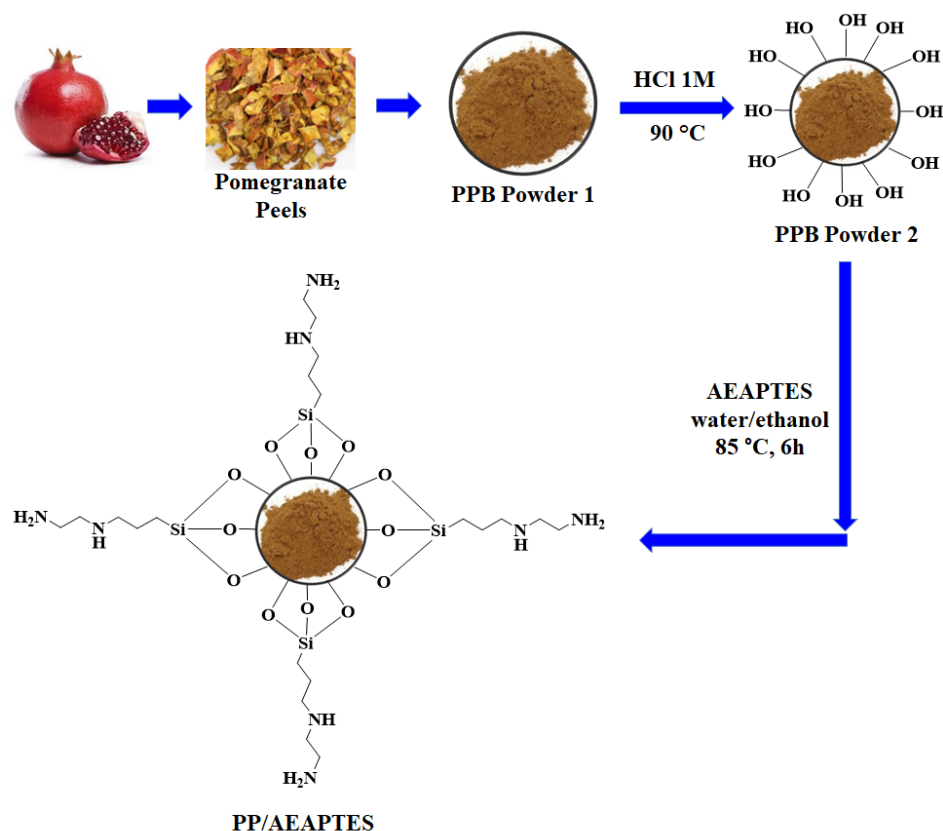


Figure 2. General scheme of the preparation of PP/AEAPTES.

2.2. Preparation of Nitrate and Phosphate Solutions and Measurement of Their Concentration

Nitrate and phosphate stock solutions were prepared by the dissolution of oven-dried KNO₃ (0.7218 g, 99.5% purity) and anhydrous KH₂PO₄ (0.7165 g, 99.5% purity) in deionized water and then diluted up to 1000 mL. The concentrations of nitrate and phosphate in the aqueous solution were determined by the ultraviolet screening method for nitrate ions and by the stannous chloride method for phosphate using a Varian Cary-4000 spectrophotometer at 275 and 690 nm, respectively, as described in the Standard Methods for the Examination of Water and Wastewater [65]. To measure nitrate ion concentration, HCl (1 mL, 1 N) was added to the aqueous solution to be analyzed (50 mL). Deionized water was used as a blank during the analysis. In addition, the interference of organic substances was checked through the measurement of the absorbance of the solution at 275 nm. Measurement of the phosphate concentration in the sample and standards was carried out by initially adding a solution of phenolphthalein indicator and a solution of HCl (1 N) until the pink color disappeared. Acid molybdate solution (4 mL) was then added, and the solutions were carefully stirred. Next, a solution of stannous chloride (0.5 mL) is added to each standard and sample, and the resulting solutions are thoroughly mixed. Finally, after 10 min, the absorbance of the phosphate solution is measured photometrically at 690 nm, with deionized water as a blank.

2.3. Experiment of Isothermal Absorption

Adsorption isotherms were obtained experimentally by a series of batch tests using 0.05 g PP/AEAPTES for the adsorption of nitrate or phosphate ions in solutions with different initial concentrations ($C_0 = 0.4, 1.2, 8, 16.0, 32.0$ and 64 mg/L), at pH 6 and 30 °C. The experimental protocol is carried out by adding 0.05 g of PP/AEAPTES to 100 mL of nitrate (or phosphate) solution in a polypropylene bottle with different initial

concentrations. After agitation at 30 °C for 2 h, the solutions were removed by filtration through 0.45 µm syringe nylon membrane filters, and the concentration of nitrate (or phosphate) ions in the obtained filtrate at the equilibrium was analyzed. The adsorption capacity q_e (mg g⁻¹) and removal rate (R) of PP/AEAPTES to adsorb PO₄³⁻ and NO₃⁻ anions were calculated by Equations (1) and (2), respectively:

$$q_e = \frac{C_o - C_e}{m} * V \quad (1)$$

$$R = \frac{C_o - C_e}{C_o} * 100 \quad (2)$$

where V (l) is the solution volume, m (g) is the weight of PP/AEAPTES, C_o (mg/L) is the initial concentration of the anions, and C_e (mg/L) is the aqueous-phase anion concentration at equilibrium.

2.4. Characterization of Materials

2.4.1. FT-IR, XRD, and XPS Analysis

To confirm the grafting success of AEAPTES on the surface of pomegranate peels, the PP and PP/AEAPTES materials were characterized by XPS, FT-IR, zeta potential, and XRD to investigate the spectral differences between these two materials. The overall FT-IR spectrum of PP/AEAPTES (Figure 3b) shows the appearance of new bands corresponding to new functions compared to the PP spectrum, suggesting the successful grafting of AEAPTES onto the PPB surface. In addition, the PP/AEAPTES spectrum shows stronger peaks and much wider bands than the PPB spectrum (Figure 3a). For example, new bands appear at 685 and 1375 cm⁻¹, attributable to the deformation of the N-H and C-N groups, respectively, which are derived from AEAPTES [59]. In addition, new bands appear at 1064 and 917 cm⁻¹, attributable to the vibration of Si-O-Si and Si-O-C, respectively, confirming AEAPTES grafting. On the other hand, both materials exhibit other bands related to functions typically present in materials derived from agricultural waste, such as the bands at 3426 and 2925 cm⁻¹, which refer to the vibration of O-H and C-H, respectively. Two other signals also appear at 1605 and 1082 cm⁻¹, which can be attributed to the vibration of HO-C=O and C-O, respectively [59].

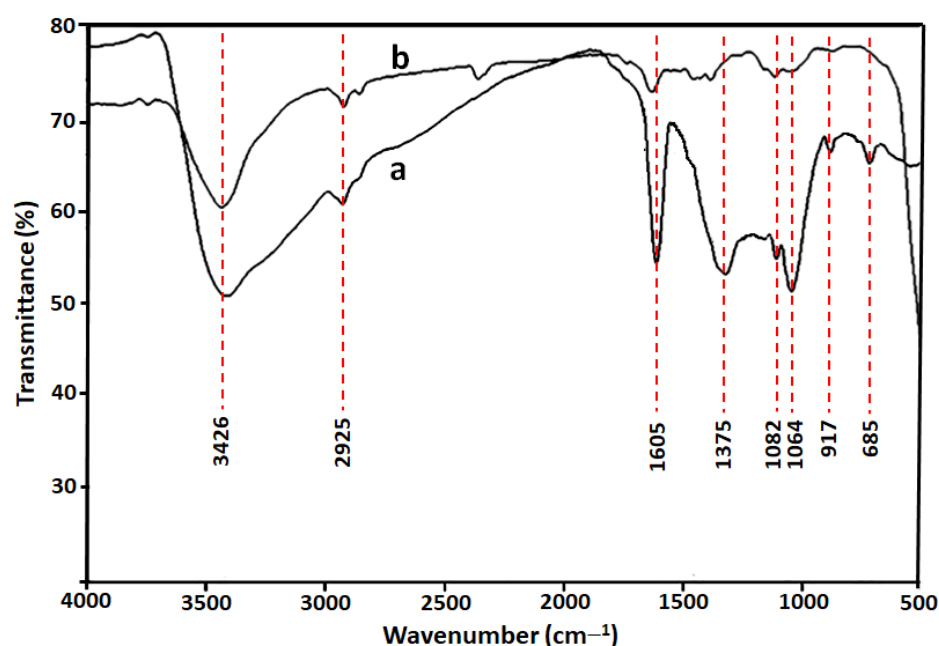


Figure 3. FT-IR spectra of (a) PPB and (b) PP/AEAPTES.

The X-ray diffraction spectrum of PPB shows a single peak with a wide aspect at $2\theta \approx 22$, as shown in Figure 4, suggesting that PPB has an amorphous structure. This result is also confirmed by the literature in which agricultural waste is generally characterized by an amorphous structure [66]. After AEAPTES grafting, PP/AEAPTES also exhibits an amorphous structure, showing that functionalization of the PPB surface by AEAPTES does not affect the amorphous structure of PPB. Thus, it is important to note that the amorphous structure of PPB remained unchanged during the functionalization process and that anions are likely to penetrate the PPB surface more readily in the amorphous region than in the crystalline region.

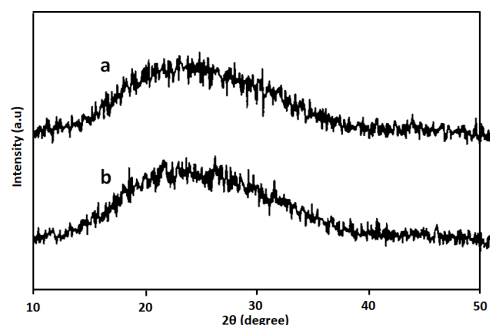


Figure 4. XRD spectra of (a) PPB and (b) PP/AEAPTES.

The surface of PP/AEAPTES was also analyzed by XPS analysis. Figure 5a shows that PPB exhibits only two strong peaks at 284 and 530 eV, attributable to the binding energies of C 1s and O 1s orbitals of carbon and oxygen, respectively. On the other hand, the PP/AEAPTES scan (Figure 5b) indicated peaks at 150 and 100, corresponding to the binding energies of the Si 2s and Si 2p orbitals, respectively. The PP/AEAPTES also showed a higher peak at 400 eV, corresponding to the N 1s orbital.

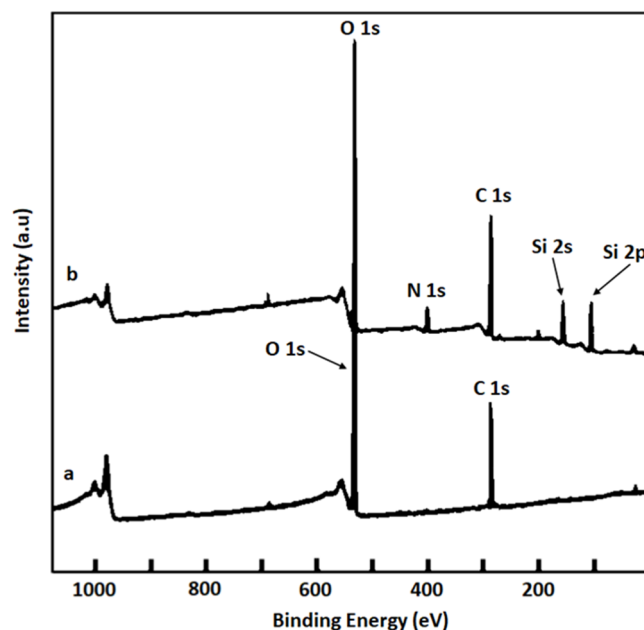


Figure 5. XPS survey scans of (a) PPB and (b) PP/AEAPTES.

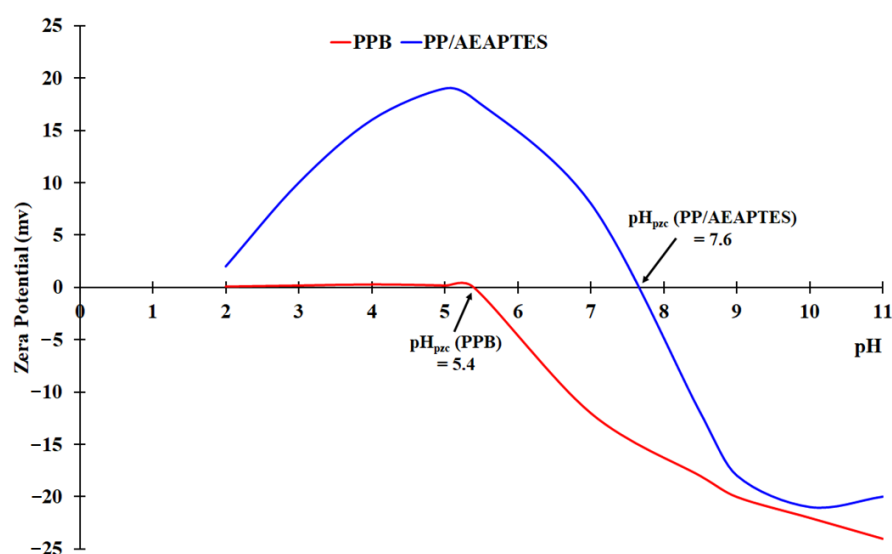
As shown in Table 1, the quantitative information obtained by XPS shows that the fraction of carbon is slightly highest in PPB (75.18%) than in PP/AEAPTES (69.78%), whereas the fraction of oxygen and nitrogen are greatest in PP/AEAPTES. These results support the success of AEAPTES grafting onto the PPB surface.

Table 1. XPS composition (at%) of PPB and PP/AEAPTES.

Samples	Elements			
	C1s	O1s	N1s	Si p ²
PPB	75.18	21.85	2.97	
PP/AEAPTES	69.78	22.64	3.54	4.04

2.4.2. Zeta Potentials and Isoelectric Points

The surface acidity of the PPB and PP/AEAPTES adsorbents was determined by measuring their zero charge points. As shown in Figure 6, both materials have a pH_{pzc} of 5.4 for PPB and 7.6 for PP-APTES. At pH < pH_{pzc}, the PPB surface is positively charged with a low zeta potential. In contrast, at pH > pH_{pzc}, the PPB surface exhibits a negative charge, and its zeta potential reaches values of −22 and −24 mV at pH 10 and 11, respectively. The changes in the electrical charge of RPP particles with pH are due to (−COOH) and (−OH) functions present in abundance in RPP. At pH > pH_{pzc}, PPB particles are negatively charged because of the ionization/deprotonation of the −COOH and −OH functions to carboxylate −COO[−] and alkolate −O[−]. However, at pH < pH_{pzc}, the COOH and OH groups are protonated, and the PPB particles become positively charged. In the case of PP/AEAPTES, pH_{pzc} analyses show that AEAPTES treatment of PPB makes the PP/AEAPTES surface positive over a pH range of 2–7.6, which is wider than what was observed for PPB. Consequently, the pH_{pzc} data confirm that the amine groups were grafted to the surface of RPP successfully. At pH < pH_{pzc} (7.6), the PP/AEAPTES surface is charged positively, which favors anion adsorption. In this respect, nitrate and phosphate capture by PP/AEAPTES should be appropriate at a pH lower than pH_{pzc} (7.6).

**Figure 6.** Zeta potential values of PPB and PP/AEAPTES versus pH.

3. Results and Discussion

3.1. Study of the Adsorption Parameters

3.1.1. Effect of the pH

The pH of the ionic solution essentially influences the chemical form of NO₃[−] and PO₄^{3−} as well as the electrical charge of the PP/AEAPTES surface. In this regard, the influence of initial pH on the capture of NO₃[−] and PO₄^{3−} ions was evaluated using raw PP and PP/AEAPTES. Firstly, Figure 7 shows that the capacity of PPB to adsorb anions is extremely low to that of PP/APTES, which explains the interest in grafting AEAPTES onto the surface of PPB. For this reason, we consider that it is not justified to use PPB in other adsorption studies. In addition, PP/AEAPTES has a high adsorption capacity for NO₃[−]

and PO_4^{3-} , which increases with the pH of the solution, reaching the maximal value of 124.57 mg g^{-1} (for NO_3^-) and 94.65 mg g^{-1} (for PO_4^{3-}) with pH 6. However, the capacity of adsorption decreases when pH increases above pH 6.

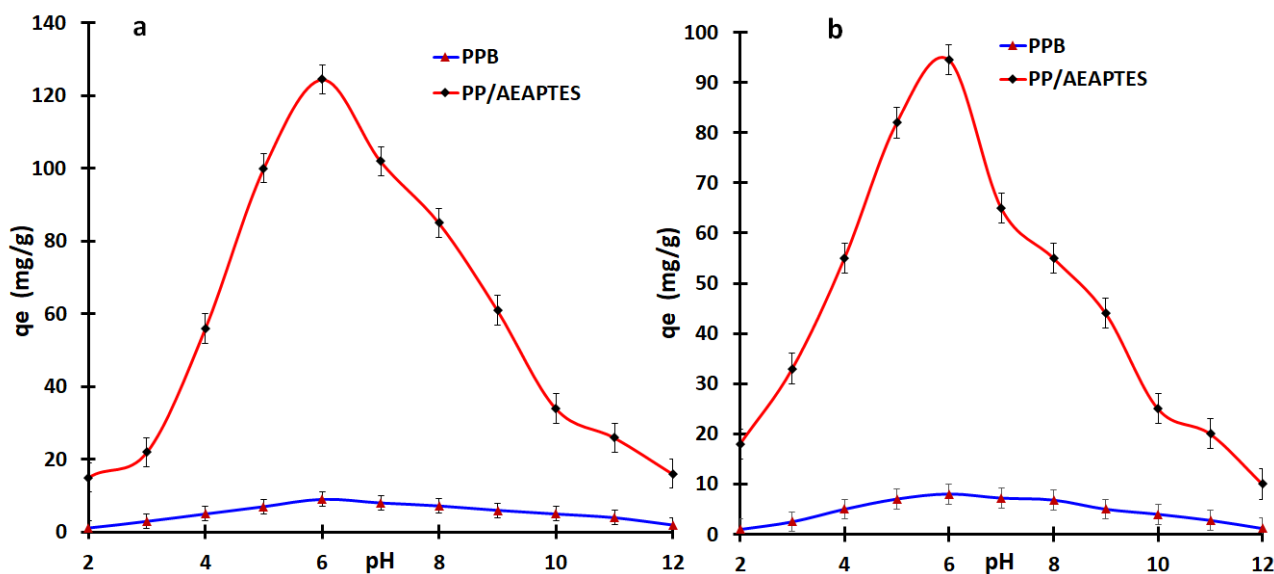


Figure 7. Effects of initial pH on (a) NO_3^- and (b) PO_4^{3-} adsorption.

As shown in the zeta potential study (Figure 6), the positive charge of PP/AEAPTES observed at $\text{pH} < \text{pH}_{\text{pzc}}$ (7.6) favors the adsorption of NO_3^- and PO_4^{3-} anions through the electrostatic interaction between these anions and PP/AEAPTES at this pH range. The capture of NO_3^- is affected by the chemical transformation of this anion as a function of solution pH. In fact, at $\text{pH} < 6$, the low adsorption of NO_3^- anions is due to the chemical transformation of NO_3^- to N_2O , despite the positive charge of PP/AEAPTES in this pH range. On the other hand, at $\text{pH} > 6$, NO_3^- decomposes to N_2 and N_2O , which also explains the low NO_3^- adsorption [67]. However, there was maximum adsorption of NO_3^- at pH 6. With respect to phosphate anions, these ions exhibit 3 pKa values ($\text{pKa}_1 \approx 2.15$, $\text{pKa}_2 \approx 7.20$, and $\text{pKa}_3 \approx 12.5$). Depending on the pH of the solution, the phosphate ions are present as H_3PO_4 (at $\text{pH} < 2$), H_2PO_4^- (at $\text{pH} 2\text{--}7$), HPO_4^{2-} (at $\text{pH} 7\text{--}11$), and PO_4^{3-} (at $\text{pH} > 11$) [68]. Figure 7 indicates that phosphate ions adsorption reached its highest value, 94.65 mg g^{-1} , at pH 6. At $\text{pH} < 6$, the primary and secondary amine groups protonate to $-\text{NH}_2^+$ and $-\text{NH}_3^+$, respectively, giving a positive charge to the PP/AEAPTES surface and thus facilitating the adsorption of H_2PO_4^- ions by the PP/AEAPTES due to the electrostatic interaction between these ions and the $-\text{NH}_2^+$ and $-\text{NH}_3^+$ groups on the surface of the PP/AEAPTES. In contrast, at $6 < \text{pH} < 7.6$, a decrease in phosphate adsorption capacity was observed due to competition between OH^- and PO_4^{3-} ions during the adsorption process. Finally, at $\text{pH} > 7.6$, the primary and secondary amine functions deprotonate, and the surface of PP/AEAPTES shows a negative charge. This negative charge, as well as the competition between NO_3^- and PO_4^{3-} , and OH^- ions, explains the downturn in the adsorption ability of NO_3^- and PO_4^{3-} anions in this pH range.

3.1.2. Effect of Adsorbent Dose

The effect of adsorbent dose was evaluated between 50 and 400 mg. The results presented in Figure 8 show that the adsorption capacity of nitrate and phosphate ions increases progressively with the amount of adsorbent, reaching a maximum of nitrate (124.57 mg g^{-1}) and phosphate (94.65 mg g^{-1}) adsorption at a dose of 0.2 g of adsorbent. Above the dose of 0.2 g, the adsorption capacity of nitrate and phosphate ions remains stable without any significant change. Thus, it is preferable to work with adsorbent doses

lower than 0.2 g to limit the risk of ineffective overdosing. In the next part of the work, we chose to work with adsorbent doses of 200 mg.

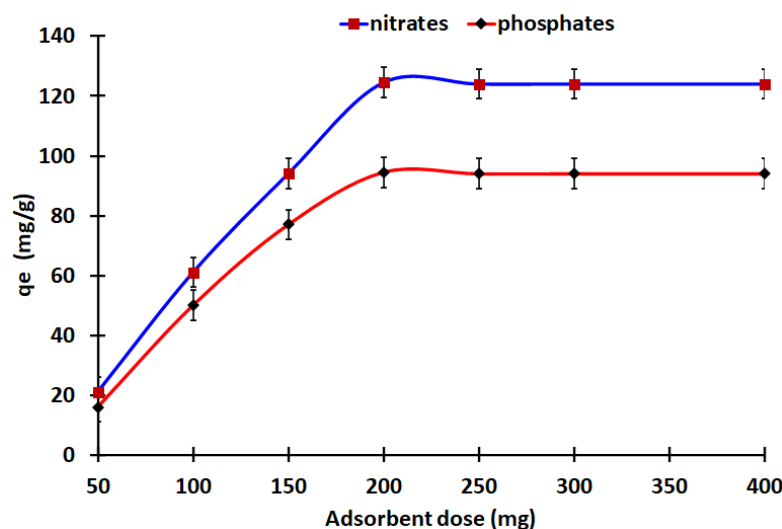


Figure 8. Effects of adsorbent dose on the adsorption of NO_3^- and PO_4^{3-} .

The increase in the adsorption capacity q_e of phosphate and nitrate ions with increasing PP/AEAPTES dose up to the value of 0.2 g is due to the increase in active binding sites, constituted by primary $-\text{NH}_2$ and secondary $-\text{NH}$ amine functions) and surface area as the adsorbent dose increases. Above 0.2 g, the adsorption capacity (q_e) decreases slightly, probably indicating the presence of another interaction phenomenon between PP/AEAPTES and ions. This could be competition between the sites retaining the ionic groups and the free PP/AEAPTES sites available to adsorb the fixed ions, causing their release into solution. This result is in accordance with our previous work [36]. On the other hand, increasing PP/AEAPTES leads to a significant increase in the adsorption capacity of NO_3^- and PO_4^{3-} ions, which rises from 21 to 124 mg g^{-1} for NO_3^- and from 16 mg g^{-1} to 94 mg g^{-1} for PO_4^{3-} , when the dose varies from 50 to 400 mg (Figure 8). The significant increase in q_e with increasing PP/AEAPTES dose is probably due to the presence of an increase in free adsorption sites ($-\text{NH}_2$ and $-\text{NH}$ amine functions) on the PP/AEAPTES surface capable of adsorbing free nitrate and phosphate ions in solution.

3.1.3. Temperature Effect

The influence of temperature was studied between 298 K and 323 K. The choice of this temperature range is due to the temperature of wastewater, which generally varies between 298 K and 323 K. The results obtained in Figure 9 show that for all studied concentrations of NO_3^- and PO_4^{3-} , the increase in temperature of the adsorption mixture from 298 to 313 K does not significantly affect the adsorption capacity of PP/AEAPTES to adsorb NO_3^- and PO_4^{3-} ions. However, a slight increase in the q_e at 323 K is observed.

The slight increase in the adsorption of NO_3^- and PO_4^{3-} ions due to the increase in temperature up to 323 K observed in Figure 9 could be associated with the endothermic aspect of the chemical reaction between the amine functions $-\text{NH}_2$ and $-\text{NH}$ linked to the surface of PP/AEAPTES and the NO_3^- and PO_4^{3-} ions [69]. On the other hand, at higher temperatures, there is an increase in ion mobility potentials, producing a swelling effect on the internal structure of the pomegranate peel, which also allows NO_3^- and PO_4^{3-} ions to penetrate the internal zones of the pomegranate peel of the adsorbent that are rich in $-\text{OH}$ hydroxyl functions [69]. The above study of the influence of temperature on the ability of PP/AEAPTES to adsorb NO_3^- and PO_4^{3-} ions shows that PP/AEAPTES can be used effectively as an adsorbent for these ions over a wide temperature range.

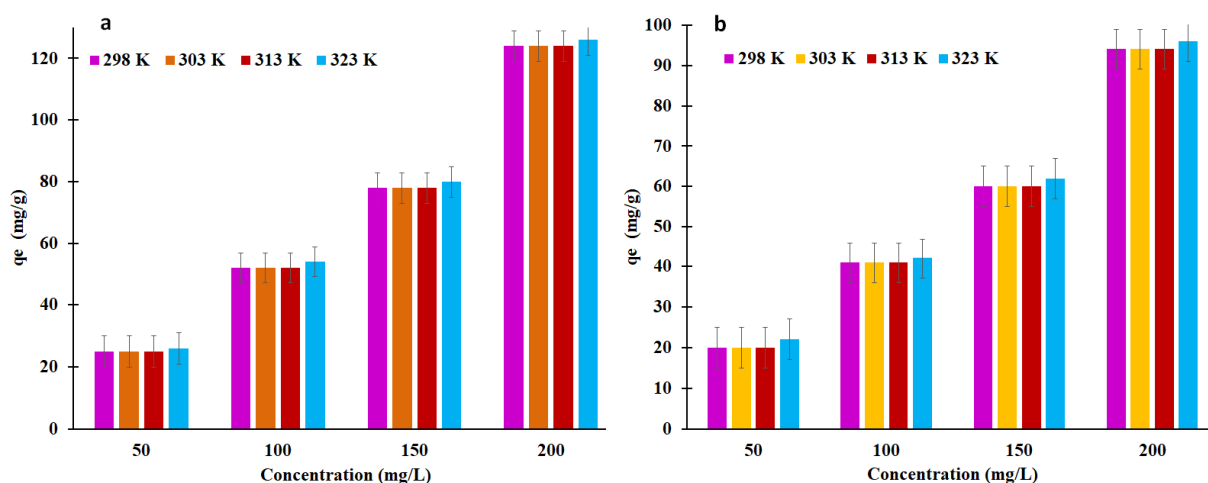


Figure 9. Effects of the temperature on the adsorption of (a) NO_3^- and (b) PO_4^{3-} .

3.1.4. Effects of Initial Anion Concentration and Contact Time

The Influence of the contact time between the NO_3^- and PO_4^{3-} ions and the adsorbent was studied at different ion concentrations to evaluate the time needed for the absorption of the maximum amount of ions by the PP/AEAPTES. As shown in Figure 10, the quantity of ions adsorbed by PP/AEAPTES increases proportionally to the concentration of ions for all the studied concentrations. However, this capacity reaches its maximum in 90 min for NO_3^- and 120 min for PO_4^{3-} for concentrations between 50 and 250 mg L^{-1} , i.e., a maximal capacity of adsorption of $124.57 \text{ mg g}^{-1}/90 \text{ min}$ for NO_3^- and $94.65 \text{ mg g}^{-1}/120 \text{ min}$ for PO_4^{3-} .

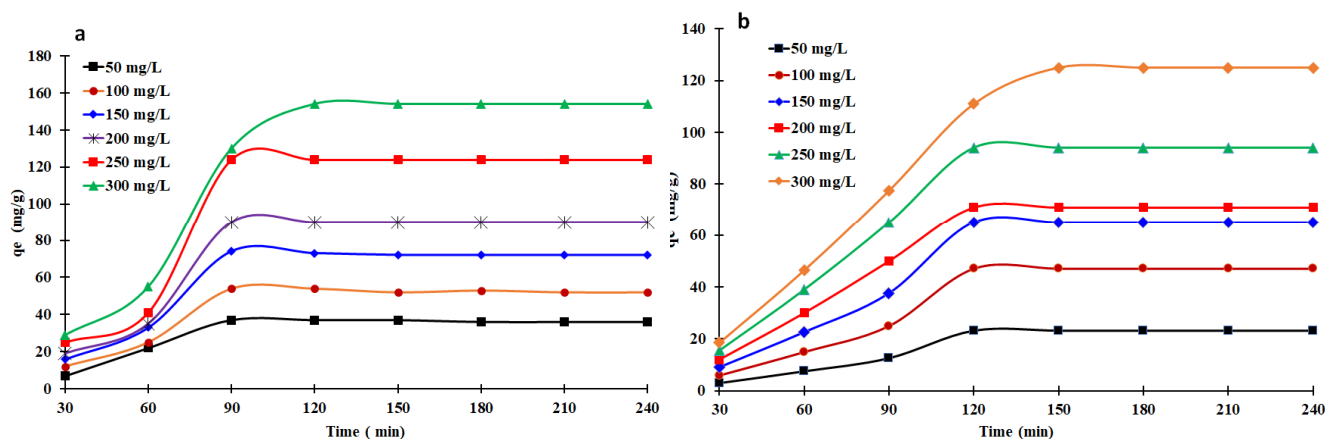


Figure 10. Effects of the contact time and initial concentration on the adsorption of (a) NO_3^- and (b) PO_4^{3-} .

The increase in adsorption capacity observed with the increase in the concentration of ions (Figure 10) is potentially due to the strong concentration gradient between the bulk surface and that of the adsorbent, generating a driving force for moving NO_3^- and PO_4^{3-} ions to the active adsorption sites (primary and secondary amines). We note that the difference between the adsorption capacity and the equilibrium time of NO_3^- and PO_4^{3-} ions is probably due to the nature of the interactions between PP/AEAPTES and NO_3^- ions, which are stronger than those with PO_4^{3-} ions. This explains the higher capacity of PP/AEAPTES to adsorb NO_3^- ions than PO_4^{3-} ions.

3.1.5. Effect of the Co-Existing Ions

The influence of the presence of co-existing ions such as Cl^- , SO_4^{2-} , Br^- , and CO_3^{2-} in the NO_3^- and PO_4^{3-} ion solution was evaluated to simulate their adsorption under real

conditions. As reported in Figure 11, the adsorption capacity of NO_3^- and PO_4^{3-} ions decreases with the increasing concentration of Cl^- , SO_4^{2-} , Br^- , and CO_3^{2-} up to a concentration of 200 mg L^{-1} . Above this value, q_e of NO_3^- and PO_4^{3-} ions remains constant.

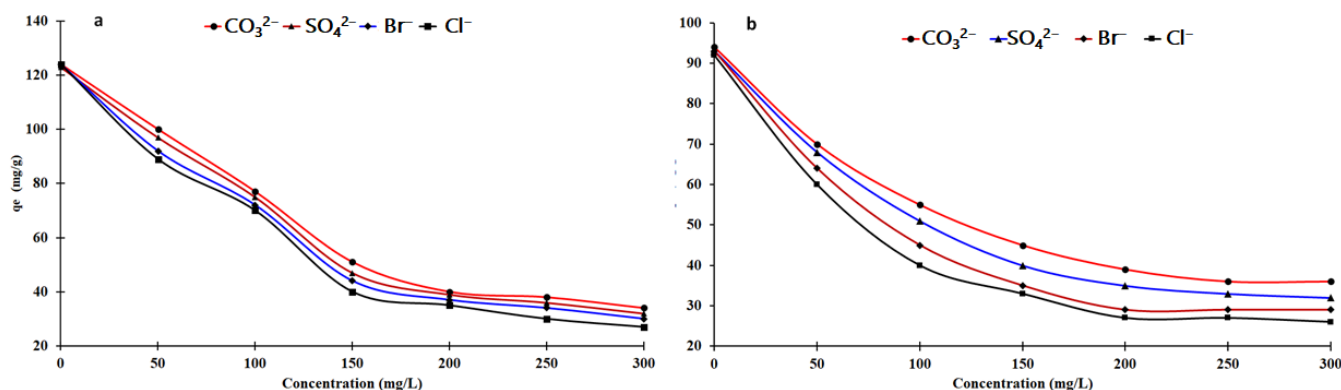


Figure 11. Effects of the other anions on the adsorption of (a) NO_3^- and (b) PO_4^{3-} .

The decrease in the adsorption capacity q_e of nitrate and phosphate ions with increasing concentrations of coexisting ions (Cl^- , SO_4^{2-} , Br^- , and CO_3^{2-}) may be due to the non-specificity of the amine functions of PP/AEAPTES for the adsorption of NO_3^- and PO_4^{3-} ions, as well as to the intensification of ionic strength when the concentration of Cl^- , SO_4^{2-} , Br^- , and CO_3^{2-} , which can inhibit ionic activity and thus limit the electrostatic interaction between the $-\text{NH}_2^+$ and $-\text{NH}_3^+$ groups available on the PP/AEAPTES surface and NO_3^- and PO_4^{3-} ions [69]. Additionally, the removal of NO_3^- and PO_4^{3-} ions decreased significantly with increasing bicarbonate concentration from 0 to 300 mg L^{-1} because increasing its concentration should raise the pH of the solution above the optimum pH, whereas the decrease in its removal with increasing sulfate concentration could be due to a high charge density of sulfate compared to nitrate and phosphate [54]. Further, the sulfate ion has the potential to form inner and outer sphere complexes, unlike nitrate, which forms only the outer sphere complex and is a weakly binding anion. On the other hand, the results reported in Figure 11 show that monovalent ions (Cl^- and Br^-) reduce adsorption capacity more than bivalent ions (SO_4^{2-} and CO_3^{2-}). This result can be attributed to the greater affinity of Cl^- and Br^- anions for the $-\text{NH}_2^+$ and $-\text{NH}_3^+$ available on the PP/AEAPTES surface than for SO_4^{2-} , CO_3^{2-} on the basis of the valence similarity between these ions.

3.2. Performance of PP/AEAPTES: Bibliographic Comparison

The adsorption experiments for NO_3^- and PO_4^{3-} anions carried out successfully on PP/AEAPTES showed unequivocal and satisfactory elimination performance. To evaluate the performance of PP/AEAPTES in adsorbing NO_3^- and PO_4^{3-} compared to other amino-functionalized adsorbents of these ions, Table 1 presents a comparison between PP/AEAPTES and other adsorbents cited in the literature on the basis of maximal capacity of adsorption (q_{max}), which is one of the main parameters to consider in the evaluation of adsorbent performance. As Table 2 shows, the q_{max} of PP/AEAPTES on NO_3^- and PO_4^{3-} anions is higher compared to other existing adsorbents.

Table 2. Comparison of NO_3^- and PO_4^{3-} adsorption capacities of PP/AEAPTES with other adsorbents.

Adsorbents	Adsorbate	Conditions	q_e (mg g^{-1})	Ref.
Tri-alkyl-amine functionalized polystyrene	NO_3^-	pH 7	44.92	[28]
Biochar-supported aluminum-substituted goethite	NO_3^-	pH 4–8	96.14	[31]
Magnetite-silica-chitosan-amine nanoparticles	NO_3^- PO_4^{3-}	pH 6 pH 5–6	112.5 89.95	[36]
Activated carbon-supported zinc ferrite	NO_3^- PO_4^{3-}	Acidic pH	75.58 91.80	[37]
Amine-Grafted Magnetic Chitosan (AFMCS) Composite Beads	NO_3^- PO_4^{3-}	pH 5 pH 7	38.40 49.95	[40]
Modified hazelnut shells with ethylenediamine	NO_3^-	pH 4–7	25.79	[56]
Branched polyethyleneimine grafted onto porous rice husk silica.	PO_4^{3-}	pH 4.5	123.46	[57]
Pomegranate Peels functionalized AEAPTES	NO_3^- PO_4^{3-}	pH 6 pH 5–6	124.57 94.65	This work

3.3. Adsorption Isotherms

To study the nature of the binding between the PP/AEAPTES surface and the adsorbate in the solid/liquid interphase, adsorption isotherms and their corresponding parameters were described by Temkin [70,71], Sips [72], Dubin-Radushkevich [73,74], Freundlich [75], and Langmuir [76] at 298 K and pH6 and at increased initial ion concentrations (from 50 to 200 mg L^{-1}). Table 3 clearly shows that the Langmuir isotherm was the adequate model for the adsorption of NO_3^- and PO_4^{3-} onto PP/AEAPTES, due to the high adsorption capacity values of 93.8587 mg/g (for PO_4^{3-}) and 124.9854 mg/g (for NO_3^-), as well as the high R^2 correlation coefficient values of 0.9986 and 0.9974, for NO_3^- and PO_4^{3-} , respectively.

Table 3. Isotherms of PP/AEAPTES for NO_3^- and PO_4^{3-} adsorption.

Isotherm Models	Parameter	Value (Phosphate)	Value (Nitrate)
Langmuir	q_{max} (mg/g)	93.8587	124.9854
	K_L (L/mg)	0.0748	0.0325
	R^2	0.9974	0.9986
	R_L	0.19682	0.2941
Freundlich	K_F (mg/g) (L/mg) ^{1/n}	5.0088	7.5312
	n_F	2.6568	3.1248
	R^2	0.8766	0.9025
	R^2	0.8843	0.8987
Temkin	K_T (L/mg)	2.6614	3.4296
	B (J/mol)	55.7784	66.776
	R^2	0.8843	0.8987
	R^2	0.9017	0.9235
Dubinin–Radushkevich	q_s (mg/g)	77.4684	112.5475
	K_{DR} (mol^2/J^2)	$3.65 \cdot 10^{-6}$	$7.75 \cdot 10^{-6}$
	E (kJ/mol)	3.1745	3.7025
	R^2	0.9017	0.9235
Sips	q_m (mg g^{-1})	87.2875	110.6284
	K_S (L mg^{-1})	0.0924	0.102
	n	2.2254	3.3875
	R^2	0.9235	0.9481
	RMS	11.7045	13.9845

In addition to the adequacy of the Langmuir isotherm model to describe NO_3^- and PO_4^{3-} adsorption on PP/AEAPTES, the study of the adsorption isotherms reported in Table 3 shows that the affinity constant (K_L) presents low values of 0.0325 and 0.0748 for NO_3^- and PO_4^{3-} ions, respectively, indicating that the adsorption process for these ions is reversible. Furthermore, the R_L values of 0.2941 and 0.19682 for NO_3^- and PO_4^{3-} , respectively (Table 3), indicate that the adsorption process for these ions onto PP/AEAPTES is favorable. According to the low values of the adsorption energy of NO_3^- and PO_4^{3-}

ions calculated on the basis of the Dubinin–Radushkevich (D–R) model, which are less than 20 kJ/mol [77] and of the Temkin heat of sorption values (B), the adsorption of NO_3^- and PO_4^{3-} ions on PP/AEAPTES is considered as being principally physisorption due to electrostatic interactions between NO_3^- and PO_4^{3-} ions and the $-\text{NH}_3^+$ and $-\text{NH}_2^+$ functions of PP/AEAPTES. On the other hand, the high values of (K_F) and (n_F) of PP/AEAPTES, estimated from the Freundlich model, confirm that PP/AEAPTES exhibits a high capacity for the adsorption of NO_3^- and PO_4^{3-} ions [78].

3.4. Adsorption Thermodynamics

The thermodynamic properties of the adsorption of NO_3^- and PO_4^{3-} ions onto PP/AEAPTES were studied by calculating the enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) based on the equilibrium constant at different temperatures (298, 308 and 318 K) and with an initial anion concentration of 150 mg L⁻¹. The results reported in Table 4 show that the ΔG values decrease progressively (more negative) with the increase in the temperature for the adsorption of NO_3^- and PO_4^{3-} , which indicates that the adsorption process of these ions on the PP/AEAPTES is of spontaneous nature and more favored between 303 and 323 K [79,80]. The positive entropy values for NO_3^- and PO_4^{3-} adsorption indicate an increase in the random nature and disorganization at the solid/liquid interface between the anions and the PP/AEAPTES. On the other hand, the enthalpy ΔH° shows a negative value (−5.42 KJ/mol) for NO_3^- adsorption and a positive value (+10.91 KJ/mol) for PO_4^{3-} adsorption, indicating that the adsorption of NO_3^- and PO_4^{3-} ions is exothermic and endothermic in nature, respectively. Furthermore, the physical adsorptions obtained on the basis of the adsorption energy value of NO_3^- and PO_4^{3-} ions calculated by the Dubinin–Radushkevich (D–R) model, and the Temkin heat of sorption (B) values are confirmed by the $\Delta H < 40$ kJ/mol values.

Table 4. Thermodynamic parameters of NO_3^- and PO_4^{3-} adsorption onto PP/AEAPTES.

Anions	ΔG° (KJ/mol)			ΔH° (KJ/mol)	ΔS° (J/Kmol)
	203 K	313 K	323 K		
NO_3^-	−4.23	−4.42	−4.81	−5.42	+40.09
PO_4^{3-}	−8.62	−9.04	−9.45	+10.91	+54.23

3.5. Adsorption Kinetics

The adsorption kinetics of NO_3^- and PO_4^{3-} ions onto PP/AEAPTES as a function of time is investigated based on four mathematical models of adsorption kinetics, i.e., The pseudo-first-order (PS-I), the pseudo-second-order (PS-II), the Elovich model, and the intra-particle diffusion model. The obtained results are summarised in Figure 12. Further, the kinetic parameters calculated on the basis of these adsorption kinetic models are presented in Table 5. Based on the R^2 correlation coefficient values, the pseudo-second-order kinetic model has the highest R^2 values (greater than 0.999) compared to the other models. In addition, the $q_e(\text{cal})$ values calculated from the pseudo-second-order model are significantly similar to those obtained experimentally $q_e(\text{exp})$. Therefore, the adsorption of NO_3^- and PO_4^{3-} onto PP/AEAPTES corresponded to the PS-II kinetic model with high correlation coefficients (R^2) compared to PS-I, Elovich, and intra-particle diffusion. These results indicate that the adsorption of NO_3^- and PO_4^{3-} ions on PP/AEAPTES involves chemisorption as well as physisorption through physicochemical interactions between the adsorbate (NO_3^- and PO_4^{3-}) and the adsorbent (PP/AEAPTES).

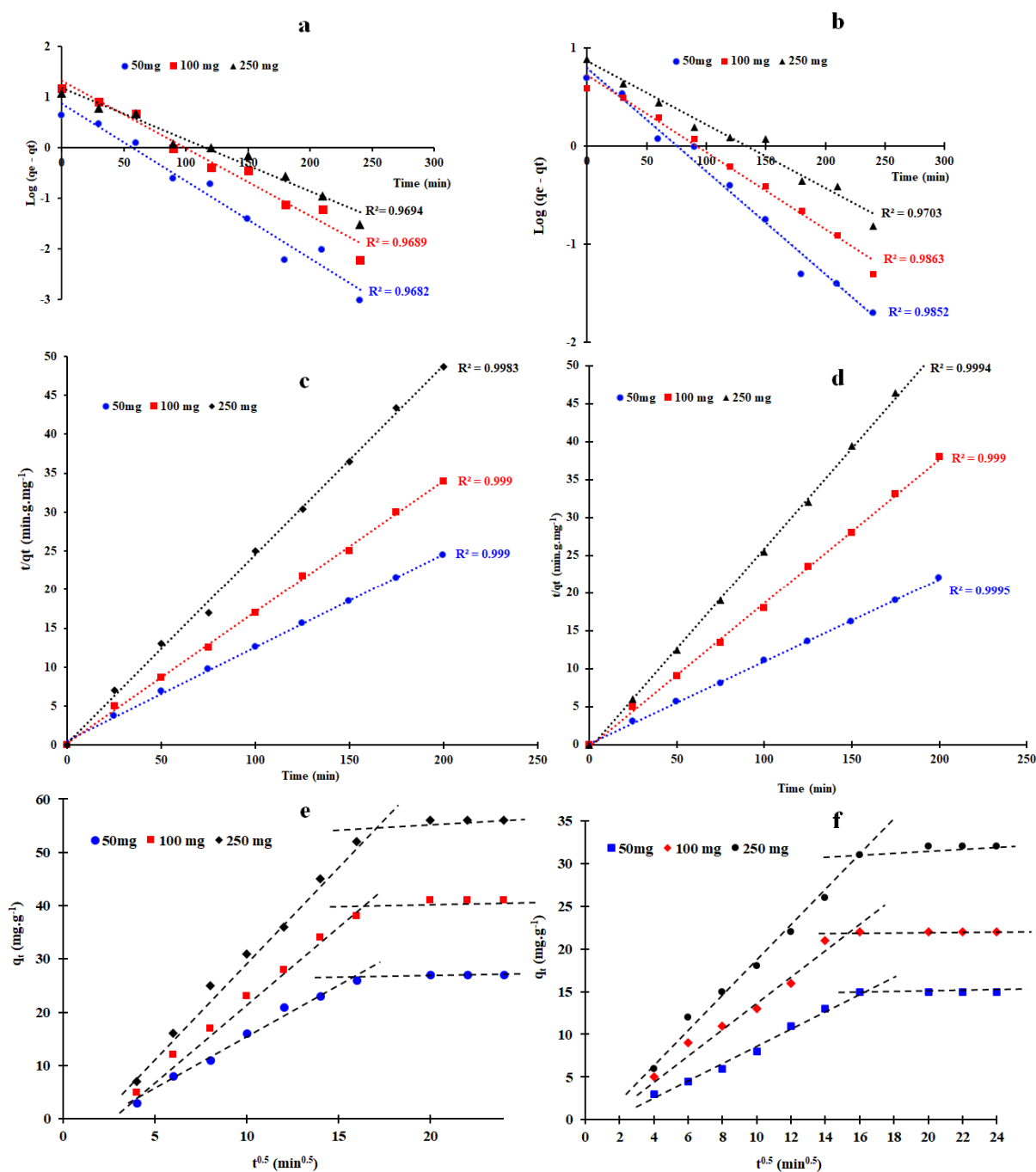


Figure 12. PS-I order (a,b), PS-II order (c,d), and intra-particle diffusion (e,f) models of NO_3^- and PO_4^{3-} adsorption onto PP/AEAPTES.

On the other hand, the mass transfer of NO_3^- and PO_4^{3-} is adequately described by the intra-particle diffusion model, according to the value of the calculated coefficient reported in Table 5. In addition, Figure 12e,f shows that two linear parts appear in all the plots, indicating that the adsorption of NO_3^- and PO_4^{3-} ions onto PP/AEAPTES involves two steps. As shown in Table 5, the correlation factor for NO_3^- and PO_4^{3-} anions ranges from 0.9558 to 0.9611 (for NO_3^-) and from 0.9712 to 0.9825 (for PO_4^{3-}), indicating that the intra-particle diffusion model may be adequate to describe the first phase of ion adsorption on PP/AEAPTES. However, the second stage of anion adsorption is slow due to the occupation of active sites on the diffusion pores of PP/AEAPTES. In addition, the

k_1 d of NO_3^- has a higher value than that of PO_4^{3-} , suggesting that the nitrate sorption process may reach equilibrium more quickly than that of phosphate ions.

Table 5. Kinetic parameters of the adsorption of NO_3^- and PO_4^{3-} ions onto PP/AEAPTES.

	NO_3^-			PO_4^{3-}		
Concentration (mg L^{-1})	50	100	250	50	100	250
q_e (exp) mg g^{-1}	37	54	124	23	47	94
Pseudo-first order						
k_1 (10^{-2}) (min^{-1})	0.0344	0.0302	0.0287	0.0227	0.0184	0.0152
q_e cal (mg g^{-1})	23.245	37.528	89.5734	17.754	33.223	58.652
R^2	0.9785	0.9711	0.9756	0.9652	0.9702	0.9646
Pseudo-second order						
k_2 (10^{-3}) ($\text{g mg}^{-1} \text{Min}^{-1}$)	0.0192	0.0125	0.0105	0.0145	0.0096	0.0064
q_e cal (mg g^{-1})	37.6587	54.8258	124.5547	23.5214	47.5324	94.6485
R^2	0.9996	0.9992	0.9998	0.9996	0.9995	0.9997
Elovich						
α ($\text{mg g}^{-1} \text{Min}^{-1}$)	21.3545	19.1254	49.3521	25.9458	35.5548	51.4355
β (g mg^{-1})	0.8573	0.6174	0.5877	0.8854	0.7998	0.8231
R^2	0.9155	0.9004	0.9354	0.9585	0.9558	0.9698
Intra-particle diffusion						
K_1 d ($\text{mg g}^{-1} \text{Min}^{1/2}$)	0.9777	1.6854	1.4585	0.5458	0.7725	0.5098
C_1 (mg g^{-1})	28.5954	39.6285	66.0585	18.6369	32.4484	50.6358
R_1^2	0.9558	0.9598	0.9611	0.9712	0.9708	0.9825
K_2 d ($\text{mg g}^{-1} \text{Min}^{1/2}$)	0.0367	0.0308	0.0158	−0.0320	−0.0034	−0.0028
C_2 (mg g^{-1})	36.8952	54.2587	113.7781	23.2585	46.9254	93.5681
R_2^2	0.6105	0.7982	0.7525	0.6998	0.45524	0.5358

3.6. Mechanism of NO_3^- and PO_4^{3-} Adsorption onto PP/AEAPTES

As the adsorption process involves both physisorption and chemisorption on PP/AEAPTES, the mechanism of adsorption of NO_3^- and PO_4^{3-} ions depends on the pH of the ionic solution. At $\text{pH} > 6$, the adsorption mechanism of NO_3^- and PO_4^{3-} ions is explained by the electrostatic interactions between these ions and the positively charged amine functions present on the surface of the PP/AEAPTES. In fact, the stable electronic configuration of the outer layer of nitrogen ($2s^2 2p^3$) gives it the possibility of forming three chemical bonds with the presence of a lone pair of electrons, which makes it a Lewis base, and at these $\text{pH} > 6$, the nitrogen atoms capture a proton and become positively charged and become $-\text{NH}_2^+$, $-\text{NH}_3^+$ and can, therefore, chemically bond to the nitrate and phosphate ions by electrostatic attraction (Figure 13).

3.7. Field Tests

The ability of PP/AEAPTES to remove nitrate and phosphate ions under real conditions was evaluated by the addition of 100 mg of PP/AEAPTES to solutions (50 mL) contaminated with phosphate and nitrate ions collected from the Casablanca region (Morocco) and the resulting data are summarized in Table 6. The initial concentration of NO_3^- and PO_4^{3-} in the initial solution before the addition of PP/AEAPTES was found to be 15.75 mg/L and 20.08 mg/L, respectively. After the addition of PP/AEAPTES (100 mg), the concentrations of NO_3^- and PO_4^{3-} decreased drastically to zero within 10 min. The drastic reduction in the concentration of NO_3^- and PO_4^{3-} ions is due to the strong electrostatic affinity between these ions and the protonated amine functions available on the surface of PP/AEAPTES. The functional reactive sites of PP/AEAPTES also reduced the

concentration of Cl^- , SO_4^{2-} , and total hardness ions that are generally present in natural water, suggesting that PP/AEAPTES is a suitable adsorbent for use in field conditions.

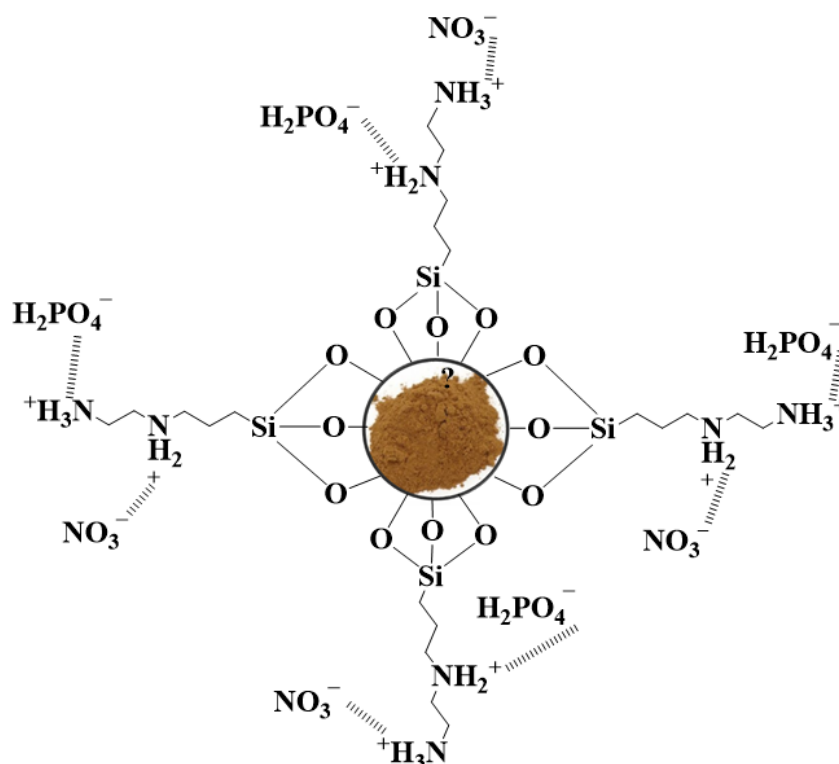


Figure 13. Mechanism of NO_3^- and PO_4^{3-} adsorption onto PP/AEAPTES.

Table 6. Field tests of PP/AEAPTES.

Parameters of the Water Quality	PP/AEAPTES	
	Before	After
pH	5.88	6.12
NO_3^- (mg/L)	15.75	Nil
PO_4^{3-} (mg/L)	20.08	Nil
Cl^- (mg/L)	235.12	131.58
SO_4^{2-} (mg/L)	168.25	102.55
Total hardness (mg/L)	598	468

The results of the elimination of NO_3^- and PO_4^{3-} ions performed on a real sample show that the adsorbent PP/AEAPTES is effective in reducing the NO_3^- and PO_4^{3-} ions concentration, as well as the concentration of other ions present in the solution (SO_4^{2-} and Cl^-), which is a major limitation of the adsorbent PP/AEAPTES. In fact, the amine functions on which NO_3^- and PO_4^{3-} are bound are not selective. Therefore, the use of PP/AEAPTES as an adsorbent for the removal of NO_3^- and PO_4^{3-} ions in large-scale real solutions can reduce the performance of PP/AEAPTES in eliminating the desired ions.

3.8. Adsorption/Desorption Cycles

Several studies report that the use of a NaOH solution is effective for the desorption of NO_3^- and PO_4^{3-} ions from an amine-functional adsorbent [36,81]. For this purpose, three solutions of NaOH with concentrations of 0.1 M, 0.25 M, and 0.3 M were used to determine the optimum concentration of NaOH solution required to desorb the maximum quantity of NO_3^- and PO_4^{3-} anions. Figure 14a shows that 92% and 89% of the NO_3^- and PO_4^{3-} ions, respectively, were desorbed with a NaOH solution concentration of 0.25 M

within 60 min. After this concentration, the desorption rate remained stable. The quasi-complete desorption of NO_3^- and PO_4^{3-} ions could suggest that these ions are weakly bound to PP/AEAPTES. The reuse of PP/AEAPTES as an adsorbent was also studied to assess the number of potential adsorption/desorption cycles. As shown in Figure 14b, after the first cycle, the adsorption rate for NO_3^- and PO_4^{3-} ions was 124.57 and 94.65 mg/g, respectively. After five adsorption/desorption cycles, this rate decreased from 124.57 to 92.14 mg/g for NO_3^- ions and from 94.65 to 65.5 mg/g for PO_4^{3-} ions. After the fifth cycle, the q_e decreased significantly to low values for NO_3^- and PO_4^{3-} ions due to the competitive effect of OH^- ions interacting with the primary and secondary functional amines of PP/AEAPTES instead of NO_3^- and PO_4^{3-} ions. As a result, PP/AEAPTES could be used without any significant decrease in removal efficiency up to five cycles, demonstrating the reusability of PP/AEAPTES to remove NO_3^- and PO_4^{3-} , and thus reducing the operating cost of the prepared adsorbent.

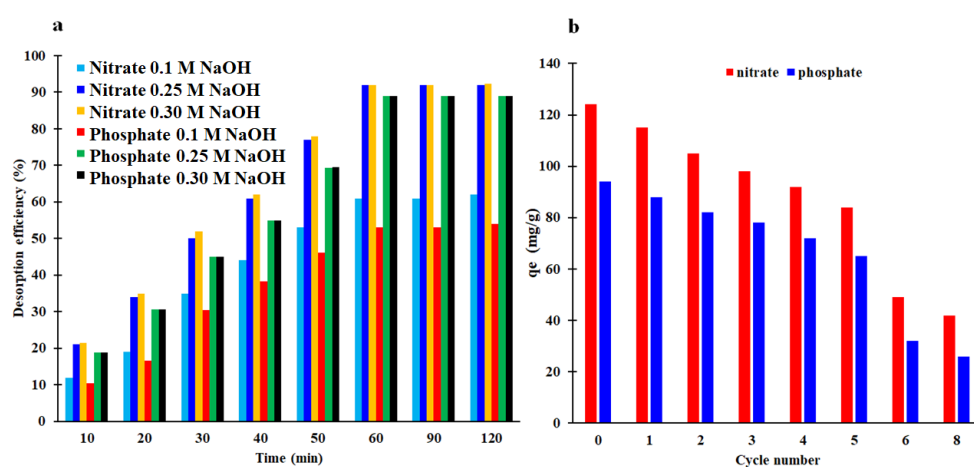


Figure 14. (a) Effect of the concentration of NaOH and the time (min) on the desorption efficacy of NO_3^- and PO_4^{3-} anions adsorbed onto PP/AEAPTES, and (b) reusability of PP/AEAPTES in repeated rounds of adsorption-desorption of NO_3^- and PO_4^{3-} .

4. Conclusions

The development of functional materials for pollutant removal is becoming increasingly important due to the growing demand for environmentally friendly techniques. Pomegranate peel has been used in its raw form to remove several pollutants. This is of major importance, as it not only reduces the level of pollutants in water but also improves the economic benefits of removing these pollutants from wastewater. Numerous studies have been carried out to develop a functionalized biobased adsorbent effective for various pollutants, but few have focused on nitrate and phosphate ions. For this reason, the present work focuses on the preparation of a high-performance adsorbent for removing nitrate and phosphate ions from a contaminated aqueous solution. The preparation of this adsorbent involved the chemo-grafting of AEAPTES on the surface of the pomegranate peel, which was confirmed by FT-IR, XRD, Zeta Potentials, and XPS analyses. Globally, the results of the adsorption capacity of phosphate and nitrate ions show that the capacity of raw pomegranate peel (PPB) to absorb these ions is extremely low compared to the results obtained with functionalized pomegranate peel (PP/AEAPTES), demonstrating the major interest of grafting AEAPTES onto the PPB surface. Detailed adsorption tests have shown that AEAPTES is capable of successfully absorbing 124.57 mg/g and 94.65 mg/g of NO_3^- and PO_4^{3-} ions, respectively, at pH 6 and over a large range of temperatures. This adsorption capacity is due to the protonation of the primary and secondary amine groups to $-\text{NH}_2^+$ and $-\text{NH}_3^+$, respectively, which confer a positive charge on the surface of the PP/AEAPTES and thus facilitate the adsorption of the nitrate and phosphate due to the electrostatic interaction between these ions and the $-\text{NH}_2^+$ and $-\text{NH}_3^+$ groups on the surface of the PP/AEAPTES. The presence of other ions affects the capacity of PP/AEAPTES to adsorb

NO_3^- and PO_4^{3-} ions. In fact, monovalent ions (Cl^- and Br^-) reduce the adsorption capacity more than divalent ions (SO_4^{2-} and CO_3^{2-}). Adsorption isotherm studies clearly demonstrate that the Langmuir isotherm is the more suitable model for the adsorption of NO_3^- and PO_4^{3-} on PP/AEAPTES. The thermodynamic properties indicate that the adsorption of NO_3^- and PO_4^{3-} ions on PP/AEAPTES is exothermic and endothermic, respectively, as well as spontaneous and physical in nature. The adsorption mechanism for NO_3^- and PO_4^{3-} ions is explained by the electrostatic interactions between these ions and the positively charged amine functions present on the surface of PP/AEAPTES. The regeneration performance of PP/AEAPTES was evaluated for up to 5 cycles with any significant loss of removal efficiency. Field analysis of the prepared PP/AEAPTES demonstrated its applicability in water samples contaminated with nitrates and phosphates collected from the Casablanca region (Morocco) (see Supplementary Materials).

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/su151813991/s1>. References [70,71,73–75,82–87] are cited in the supplementary materials.

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