

Research Article

Application of Raw and Modified Pomegranate Peel for Wastewater Treatment: A Literature Overview and Analysis

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The use of renewable substrates as biosorbents has a great attention in wastewater treatment. The pomegranate peel (PGP) constitutes one of these substrates. A review is carried out to investigate the potential of pomegranate peel (PGP) for wastewater treatment. Physical and chemical PGP properties are presented and compared to those of Tunisian pomegranate peel (El Gabsi). Raw and modified PGP performance and sorption capacity for metals, dyes, and organic pollutants are evaluated. Different experimental sorption conditions such as concentration, contact time, pH, temperature, and adsorbent dose used in the literature are illustrated. Studied and best-fitted kinetics and isotherm models to experimental data and thermodynamic parameters are compared. The effects of activating physical and/or chemical conditions on the activated PGP properties are presented. This paper reveals noteworthy properties of raw PGP for wastewater treatment compared to this activated form. The comparison between activated and raw PGP morphology exhibits that the activation does not necessarily improve the PGP adsorption capacity. Despite a limited research carried out on the raw PGP biosorbent, it appears from this study that it has very good adsorption properties, making it a serious and low-cost renewable substrate toward practical applications in wastewater treatment compared to various other waste agricultural biomass.

1. Introduction

Aquatic system pollution has become worldwide environmental problem. In order to overcome this concern, agricultural waste materials constitute an economical and ecological biosorbent for recovery of pollutants from wastewater. They include shells of wheat, bran, and rice [1], orange peels [2], sunflower leaf [3], olive stones [4], litchi pericarp [5], and other materials detailed in the overview [6–8]. Another less studied waste agricultural material that could be very efficient as biosorbent for pollutants removal is the pomegranate peel, a by-product of the pomegranate juice industry. Pomegranate (*Punica granatum* L., family Punicaceae) is one of the most popular fruits in the world due to its pleasant taste, high nutritional value, and many medical features. Its annual world production is estimated at about three million tons. India, Iran, and China are the most productive countries producing 900, 800, and 250 million tons, respectively [9]. There are over 1000 cultivars of

Punica granatum from the Middle East, the Mediterranean region, eastern China, India, the southwestern United States, California, and Mexico [10]. In Tunisia, pomegranate production is about 71 597 tons/year in 2010 [11]. Pomegranate fruits are widely consumed fresh and in processed forms as juice, jams, and wine. The pomegranate peel constitutes up to 30% of the fruit total weight, but it is usually discarded as a waste residue. It contains two important hydroxybenzoic acids, gallic acid and ellagic acid. It also contains hydroxycinnamic acids and derivatives of flavones. Numerous ellagitannins are also present, such as punicaline, punicalagine, corilagine, granatine A, and granatine B. These tannins represent up to 28% of pomegranate peel that can be used for anti-inflammatory, antimicrobial, and antioxidant treatment [10, 12]. These benefits of PGP constituents can be extracted for medicinal [13], dyeing [14], and adhesive applications [15], and the solid waste can be used as low-cost and renewable source of biosorbent [16–20].

However, few studies have so far been done to investigate the potential capacity of untreated and modified pomegranate peel for wastewater treatment. The purpose of this work is to present physical and chemical properties of raw Tunisian pomegranate peel (El Gabsi) and the effect of washing treatment on these properties especially on the exposed adsorption surface. Furthermore, it gives a review of the most published paper dealing with pomegranate peel biosorption. Physical and chemical characteristics of raw and activated PGP material such as moisture content, ash content, porosity, BET surface, particle density, elementary composition, and functional groups are compared. Different experimental parameters such as the pH solution, the initial metal concentration, the adsorbent dose, the particle size, and the contact time are presented. The thermodynamic, equilibrium isotherms and kinetic models are analyzed. A discussion is raised out about the need of activation for this by-product agriculture substrate.

2. Materials and Methods

2.1. Preparation and Characterization of the PGP. Pomegranate peel (PGP) was collected in the southern region of Tunisia (Gabes) named El Gabsi. It was initially washed with double-distilled water for several times. Then, it was dried in an air oven at 323 K overnight. The PGP was then characterized with the point of zero charge, TG/DTA, and FTIR spectrum analysis. The morphology structure of washed and nonwashed PGP was examined by a scanning electron microscopy (SEM) (JEOL 6360LV).

2.1.1. pH of the Adsorbent. The equilibrium pH of the PGP adsorbent was determined by placing 1 g of the PGP in 100 ml of distilled water. After shaking for 24 hours, the suspension has been filtered. The pH value of the filtrate was measured using a pH meter type Schott (CG-841 model) with a single combined electrode.

2.1.2. Point of Zero Charge (pH_{pzc}). The pH_{pzc} was determined by mixing 0.15 g of PGP adsorbent with 50 mL NaCl solution (0.01 N). The initial pH was adjusted with NaOH or HCl solution between 2 and 12. The mixture was shaken for 48 hours. The PGP adsorbent was removed by filtration, and then the pH was measured. The intersection of the bisector and the pH_{final} versus $pH_{initial}$ curve gives the point of zero charge pH_{pzc} value.

2.1.3. Fourier-Transform Infrared Analysis (FTIR). FTIR spectra were obtained by a Nicolet IR200 infrared spectrophotometer equipped with a DTGS detector in the wavelength range $4000\text{--}400\text{ cm}^{-1}$. A sample of the Tunisian pomegranate peel was deposited directly on a crystal (diamond/ZnSe) type.

2.1.4. Thermogravimetric Analysis (TGA). The thermogravimetric analyses (ATG-ATD) were carried out under a nitrogen (N_2) atmosphere using a Setaram type device

(SETSYS Evolution Ev 1750 (TGA- DTA 1600) thermal analyzer). The sample is heated between 25°C and 900°C with a speed $10^\circ\text{C}/\text{min}$. The nitrogen flow rate N_2 used is 20 ml/min. The initial mass of the sample introduced is of the order of 10 mg of pomegranate peel.

3. Physical and Chemical PGP Properties

Chemical analysis of pomegranate peel adsorbent showed that its major constituents are carbon, oxygen, and hydrogen. Tunisian PGP composition is 43.13% of carbon, 48.15% of oxygen, 7.17% of hydrogen, 0.66% of Nitrogen, and 0.89% of sulfur [17]. This composition is comparable to the Turkish PGP, which has 43.94% of carbon, 49.55% of oxygen, 4.73% of hydrogen, 1.23% of nitrogen, and 0.55% of sulfur [21]. Whereas Indian PGP composition is different, it has 35.96% of carbon, 58.38% of oxygen, 58.38% of hydrogen, 0.65% of nitrogen, and 0.09% of sulfur [22]. Moisture contents given by El-Ashtoukhyet al. 2008 is very high compared to the average literature value, and it may be probably related to fresh PGP while other encountered values are related to dried PGP [18]. The average ash contents value is less than 5%, while ash contents reported by Ben-Ali et al. 2017 are relatively high. BET surface area varied from 1.28 to $10\text{ m}^2/\text{g}$, porosity ranged between 30.88 to 60%, and particle density reported varied from 0.38 to $0.89\text{ g}/\text{cm}^3$. PGP has different properties, which probably varies with origin and region. Table 1 summarizes, from literature the PGP proximate and ultimate analysis.

The principal surface functional groups are carboxylic acid, phenol, and carbonyl. Figure 1 proves that the concentration of the acidic functions is more important than basic one on the surface of the biosorbent ($3.4\text{ meq}\cdot\text{g}^{-1}$).

pH_{pzc} value is located at the intersection point of the final pH (pH_f) vs. the initial pH (pH_i) curve and the $pH_i = pH_f$ line. The pH_{pzc} is found to be 4.7 (Figure 2). Thus, the PGP surface is positively charged for pH values below the pH_{pzc} and negatively charged for pH values higher than pH_{pzc} . Different pH_{pzc} value was reported for Turkish untreated pomegranate peel adsorbent by [24] which is equal to 6.53.

3.1. Scanning Electron Microscopy. The surface morphology of the raw and washed PGP is identified by scanning electron microscopy (SEM). Both sides of pomegranate peel as shown by Figure 3 have been analyzed. Figures 3(a) and 3(c) are the outer sides of dried raw and washed PGP, respectively. Figures 3(b) and 3(d) are the inner sides of dried raw and washed PGP, respectively. The obtained SEM images for the outer side of raw and washed PGP are roughly similar (Figure 4(a)). It is a rough surface without pores. Figure 4(b) shows a cross section of PGP. It reveals that the pores are developed at the level of the inner PGP surface. Figures 4(c) and 4(d) shows some pore development, whereas Figures 4(e) and 4(f) exhibit a great pore development of raw washed PGP. This could be explained by the tannin extraction from PGP. In our previous study [25], we showed that the PGP extract content is about 58% yield. The tannin removed releases PGP surface and provides a surface with

TABLE 1: Pomegranate peel proximate and ultimate analysis.

BET (m ² /g)	Porosity (%)	Particle density (g/cm ³)	Moisture (wt %)	Ash (wt %)	C	H	S	O-N	N	O	References
—	—	0.38	8.12	9.68	43.13	7.17	0.89	48.81	0.66	48.15	[17]
1.28	30.88	0.89	10.43	3.63	35.96	4.92	0.09	59.03	0.65	58.38	[22]
5.04	—	—	7.9	4.98	28.46	5.70	0.08	65.76	—	—	[16]
10	—	—	—	—	43.94	4.73	0.55	50.78	1.23	49.55	[21]
—	42	—	36.11	3.36	—	—	—	—	—	—	[18]
—	60	0.58	6.79	9.98	—	—	—	—	—	—	[23]

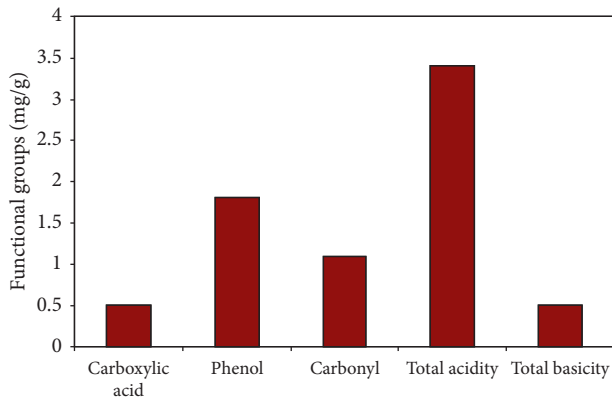
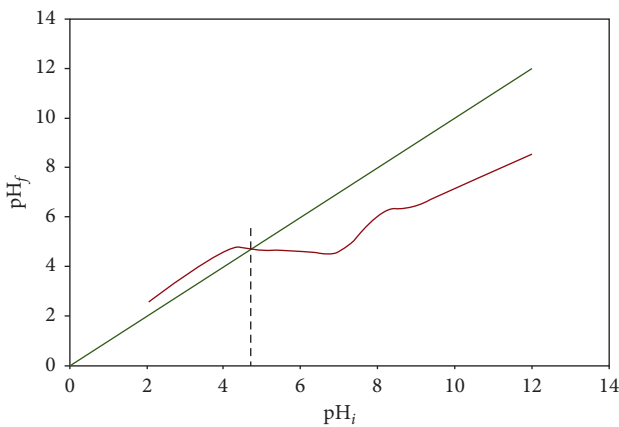


FIGURE 1: Relative contents of surface functional groups of Tunisian PGP.

FIGURE 2: Point of zero charge (pH_{pzc}) of washed Tunisian PGP.

good pore development. A great dissimilarity is observed in the SEM results obtained by the different authors regarding the PGP morphology. This is due probably to the analyzed side of the pomegranate peel. Actually, both sides of PGP are very different (inner and outer sides) as shown by Figure 3. Moreover, PGP properties varied with its origin.

Ahmad et al. [16] reported that the raw PGP surface texture is rough and uneven and does contain any pores (Figure 5(a)) [16]. Whereas Pathak et al. [22] described the surface of raw PGP by rough and uneven with some pores (Figure 5(b)). The SEM result obtained by El-Ashtoukhy et al. [18] provides more different surface morphologies (Figure 5(c)). From Rouabeh and Amrani's [26] SEM result, the PGP surface has some macropores and micropores (Figure 5(d)).

3.2. Thermogravimetric Analysis. Thermal analysis of PGP was performed by TG/DTG curves under an atmosphere of nitrogen with a heating rate of 10°C/min. The temperature scanning was conducted in the range 22–800°C with a 10 mg of Tunisian PGP biosorbent. Figure 6 shows that there are four mass losses from lower temperatures up to 500°C. The first mass loss corresponds to water and volatile organic materials loss and extends from the beginning of the analysis until the temperature of 200°C. The second mass loss corresponds to the first decomposition peak which is observed between 200°C and 300°C and is related to the presence of hemicellulose and pectin. The third peak is observed between 300°C and 400°C and corresponds to the decomposition of cellulose. Finally, a slow decomposition is observed at higher temperatures and represents the ash residues. From these results, PGP is stable and can be used as biosorbent in its raw form.

3.3. FTIR Analysis. The FTIR spectrum of analyzed PGP is shown in Figure 7. Using data from the literature, absorption bands corresponding to functional groups are attributed [24]. The band about 3280 cm⁻¹ can be assigned to the stretching vibration bond of hydroxylic groups (carboxylic acid, phenol, or alcohols). The band observed at about 2935 cm⁻¹ is assigned to the stretching vibration bond of aliphatic C-H groups. The peak around 1727 cm⁻¹ represents C=O stretching of the carbonyl group. The band at 1617 cm⁻¹ is assigned to the stretching vibration bond of C=O and C=C. The peaks at 1320 cm⁻¹ and 1020 cm⁻¹ are assigned to C-O groups of carboxylic acid, alcoholic, phenolic, ether, and ester groups. The peak at 1446 cm⁻¹ is assigned to the ring vibration. These results agree with surface functional groups determined by the Boehm titration method and are presented above (Figure 1). Thus, pomegranate peel is rich in oxygenated surface groups.

4. Adsorption on Raw and Modified PGP

4.1. Metal Removal Applications. Pomegranate peel ability for pollutants removal was studied for the first time by El-Ashtoukhy et al. [18]. The authors used raw and modified PGP as a biosorbent for the removal of lead and copper. Four forms of PGP were studied (raw, AC1, AC2, and AC3). Various activation processes were carried out after common prior treatment. PGP was washed with distilled water, dried in an oven for two hours at 105°C, and crushed and sieved to particle size range of 0.3–0.6 mm. The obtained material was divided to four parts. The first one was used as it was considered as a raw material. The second part, named AC1,

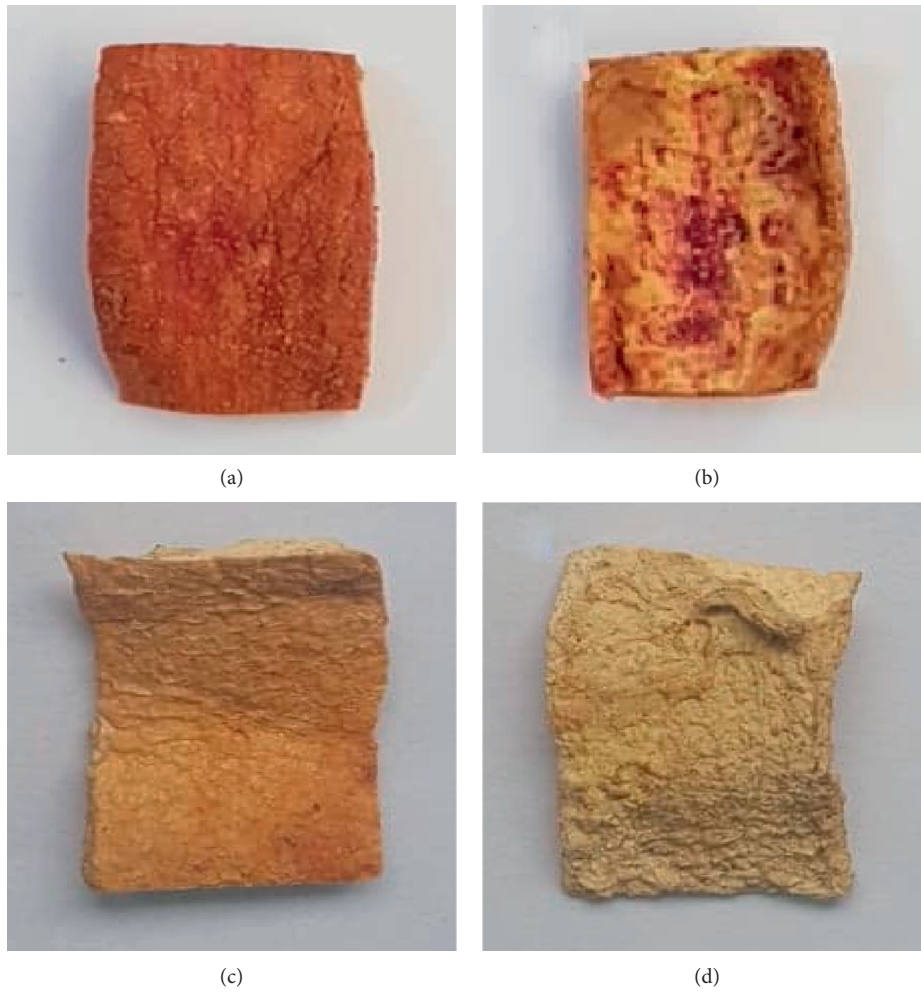


FIGURE 3: Both sides of raw (a and b) and washed (c and d) pomegranate peel (El Gabsi).

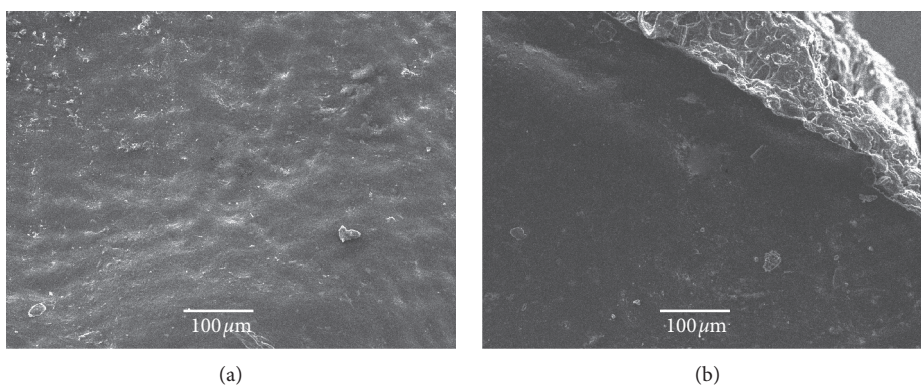


FIGURE 4: Continued.

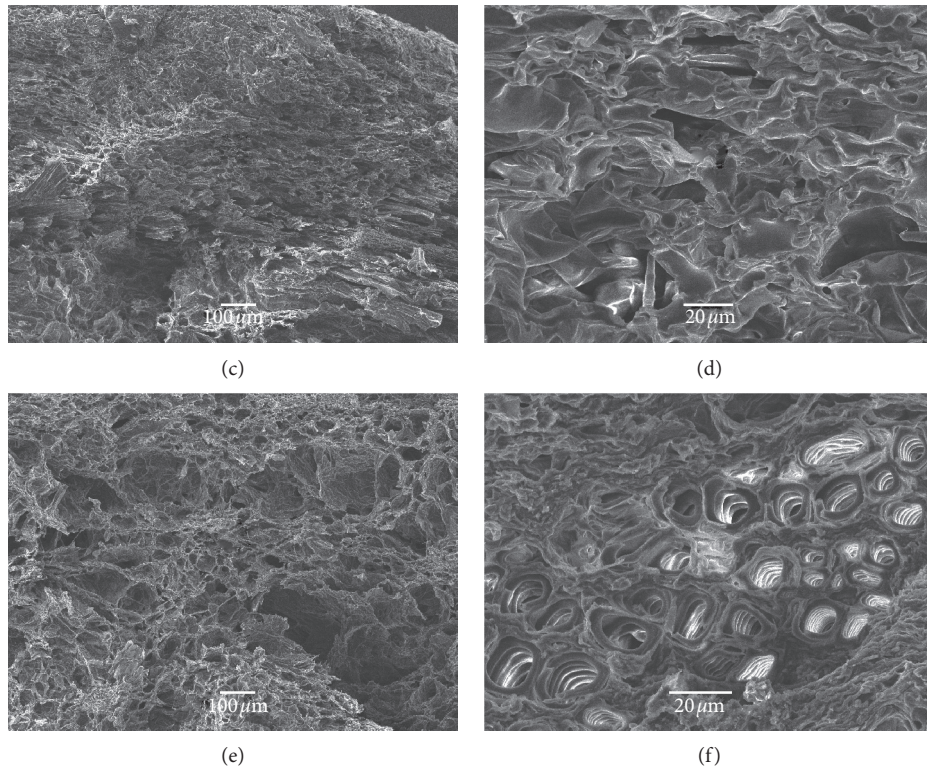


FIGURE 4: Scanning electron microscopy of raw (a b, c, and d) and washed (e and f) Tunisian PGP (El Gabsi).

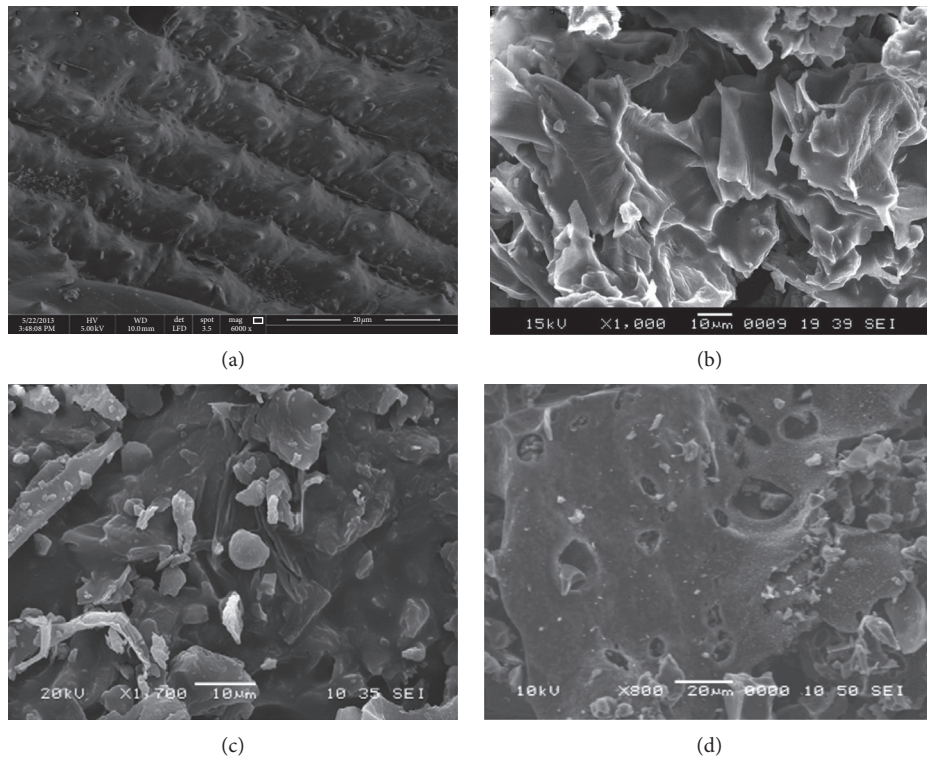


FIGURE 5: Scanning electron microscopy of PGP (a) [16], (b) [22], (c) [18], (d) [26].

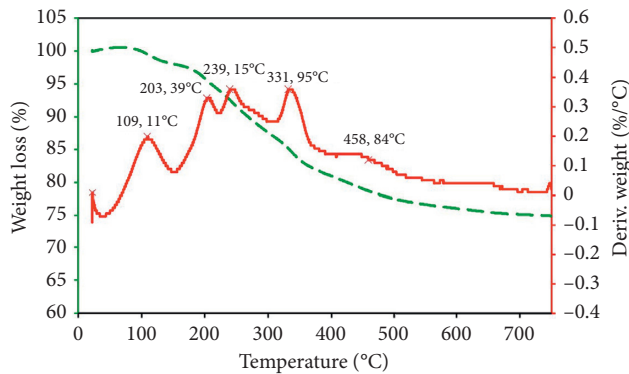


FIGURE 6: A plot of TG/DTA for the Tunisian pomegranate peel thermal behavior.

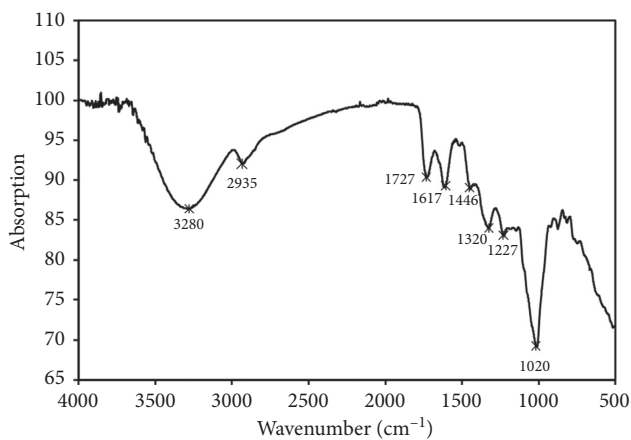


FIGURE 7: Infrared spectrum of Tunisian raw pomegranate peel.

was carbonized in absence of air at 500°C. The third part, named AC2, was soaked for twenty-four hours in a mixture of phosphoric acid and zinc chloride solution in a ratio of 1 : 1 and then dried and carbonized as AC1. The last part, named AC3, was soaked for twenty-four hours in nitric acid (10% wt) and then dried and carbonized as AC1. Physical properties of raw, AC1, AC2, and AC3 were determined. Adsorption experiments were carried in batch at room temperature. Contact time (0–200 min), pH (1–10), initial metal ion concentration (0–50 mg/L), and adsorbent concentrations (0–1.2 g/L) were studied. Optimum adsorption conditions found were contact time of 120 min, pH of 5.8, and biosorbent dose of 2.5 g/L.

Adsorption kinetics data were modeled using the pseudo-first-order, pseudo-second-order, Elovich linear equations, and intraparticle diffusion models. Adsorption isotherm used for fitting experimental data was Langmuir, Freundlich, and Temkin. The results indicated that the pseudo-second-order model gave the best fit to kinetic data. Langmuir and Freundlich models fitted isotherm adsorption data of lead and copper ions, respectively. Langmuir maximum adsorption capacity of PGP for lead and copper ions removal was found to be 17.953 mg/g and 21.978 mg/g for PC3, respectively. Whereas for raw PGP, maximum adsorption capacity was found to be 13.870 mg/g and 1.3185 mg/g for lead and copper ions, respectively. There

appears to be a great difference between adsorption capacity for copper of modified and raw PGP, while closed values were obtained for lead.

Najim and Yassin [27] investigated the use of raw and formaldehyde modified PGP for chromium (VI) removal. The biomass was first crushed and sieved to particle size of 500 μm and then soaked with distilled water for overnight and filtered. This process was repeated for ten times to remove all colored and soluble materials, which constitute more than 40% of PGP. After filtration, biomass was dried in an air oven at 80°C overnight and named MPGP. The formaldehyde-modified PGP (FMPGP) was obtained by reacting MPGP with 8% formaldehyde solution in a ratio of MPGP to formaldehyde solution 1 : 5 w/v at 60°C for 4 hours. The biosorbent particle size used was 150 μm . Adsorption experiments were carried out in batch for metal concentration in a range of 10–40 mg/L with a contact time of 100 minutes. The solution pH values studied were in a range of 1–6. Biosorbent doses used were 1, 2, 4, and 6 g/L of MPGP and 1, 2, 4, 8, and 12 g/L of FMPGP. Adsorption isotherm experiments were carried out at different temperatures (20, 30, 40, and 50°C). The optimum adsorption conditions were found to be biosorbent dose of 2 g/L, pH of 2, and equilibrium time of 80 min. The maximum adsorption capacity of MPGP and FMPGP for Cr(VI) removal was found to be 26.882 mg/g and 35.336 mg/g at 303 K, respectively. Adsorption capacity increased greatly with temperature increase to reach 323 K for 47.17 mg/g and 49.75 mg/g of MPGP and FMPGP, respectively. Results showed that the adsorption into FMPGP and MPGP is a favourable physical process; except at 50°C for MPGP, the adsorption may be chemical. Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm equations were used to fit experimental data. Results revealed that the best fit to the adsorption data of Cr(VI) onto MPGP and FMPGP was obtained with the Dubinin-Radushkevich isotherm model. From kinetic study, it was highlighted that surface adsorption and intraparticle diffusion were concurrently operating during the chromium (VI) biosorbent interaction. The pseudo-second-order kinetic models fitted adsorption data more than pseudo-first-order and Elovich models.

Nemr [28] studied the removal of chromium (VI) from aqueous solutions using chemically activated carbons prepared from PGP. The biomass was washed with distilled water and oven dried at 150°C for 3 days. The dried material was crushed and sieved to particles size of about 1.0 mm.

Activation was done by mixing PGP and 98% H_2SO_4 solution. The mixture was kept overnight at the room temperature ($25 \pm 2^\circ\text{C}$) followed by refluxing for 10 hours. After cooling to the room temperature, the reaction mixture was poured on to 6 L of cold water and filtered. The resulting material was soaked in 1% NaHCO_3 solution to remove any remaining acid. The obtained carbon was then washed with distilled water until pH 6, dried in an oven at 150°C for 48 hours in the absence of oxygen, and sieved to the particle size less than 0.063 mm. The obtained activated carbon was named PGHC. Adsorption experiments were performed at different initial pH values (1.0–10.2). It was reported that the PGHC surface is positively charged up to pH < 4,

heterogeneous in the pH range 4–6, and negatively charged above pH 6. Thus, the adsorption $\text{Cr}_2\text{O}_7^{2-}$ ions was favorable at pH lower than pH 4, and maximum chromium uptake occurred at pH 1. The adsorption contact time was studied, and the equilibrium time was found to be about 180 min. The effect of adsorbent dose was studied from 2 to 6 g/L. The adsorption capacity of PGHC decreased from 17.34 to 8.33 mg/g and from 30.57 mg/g to 21.35 mg/g by increasing the adsorbent dosage from 2 to 6 g/L at 50 mg/L and 150 mg/L Cr(VI) concentration, respectively [28]. Thus, the adsorption capacity decreased with adsorbent dose increase by keeping the Cr(VI) concentration constant. Najim and Yassin reported similar results for chromium (VI) removal by formaldehyde-modified PGP. The adsorption capacity of MPPG decreased from 5.085 to 1.314 mg/g by increasing the adsorbent dosage from 1 to 6 g/L, while, for FMPGP, the adsorption capacity decreased from 2.733 mg/g to 1.918 mg/g and from 26.873 mg/g to 2.981 mg/g, when the adsorbent dosage increased from 1 to 12 g/L at 10 mg/L and 40 mg/L Cr(VI) concentration, respectively. This observation was explained by the availability of less number of Cr(VI) ions per unit mass of the biosorbent causing the site remaining unsaturated during the adsorption process. Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R), and generalized isotherm equations were employed to find the best-fitting isotherm model. The Langmuir form and generalized models provide the highest fit to the chromium adsorption data process by PGHC. The Langmuir maximum adsorption capacity at optimum operating conditions was found to be 35.2 mg/g. Kinetic models analyzed were pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion. It was found that data were more fitted to the pseudo-second-order. Nembr [28] investigated the effects of salinity and real wastewater on the PGHC capacity for chromium adsorption. Results showed that chromium removal (%) into distilled water, synthetic sea, natural sea water, and wastewater was 85.39%, 84.02%, 83.15%, and 82.50% for PGHC, respectively. Yet, whatever the solution salinity is, PGHC is applicable for Cr(VI) removal. It was demonstrated that biosorbent could be regenerated. For that, desorption experiments were carried out at 25°C by using 0.1 N NaOH giving 95% desorption after contact time of 120 min. Activation of PGHC was achieved by mixing with 1N HCl solution for 120 min and washing with distilled water.

Abbasi et al. [29] prepared pomegranate peel for Cobalt and Nickel removal. Peels were separated from the fruit, washed thoroughly and dried in sun light for three days, and dried in an oven at 90°C. The dried PGP was crushed and sieved to a size of 200–400 μm . The solution pH effects were studied in a range (1–6). The increase of adsorbent dose from 1 to 3 g/L increased the metal ion removal from 46% to 87% and from 38% to 78% for Co (II) and Ni (II), respectively. Contact time studied were in the range of (5–60 min), and equilibrium time obtained was 35 min. Adsorption capacity of PGP for Co (II) and Ni (II) increased when pH increased; thus, pH 6 was the optimal adsorption value. Langmuir and Freundlich isotherm equations were used. Both models fitted experimental data. The maximum Langmuir

adsorption capacity of Co (II) and Ni (II) was found to be 8.98 mg/g and 7.54 mg/g, respectively. The thermodynamic study showed that the adsorption process of Co (II) and Ni (II) ions onto PGP was spontaneous and endothermic.

Najim and Yassin [27] and Rao and Rehman [30] investigated the use of raw PGP for Cu(II), Ni(II), Zn(II), Cd(II), and Cr(VI) ions removal. PGP was dried, crushed, and washed several times with doubly distilled water to remove all colored and soluble materials. Then, PGP was dried in an air oven at 60°C for 24 hours and sieved to particle size in a range 150–300 μm . Adsorption experiments were carried out in batch for copper removal and in continuous flow fixed bed column for Cu(II), Ni(II), Zn(II), Cd(II), and Cr(VI) ions removal. The maximum adsorption occurred at pH 4.5. Langmuir and Freundlich isotherm equations were used. The Freundlich model provided the better fit of experimental data. Maximum adsorption capacity of PGP for Cu(II) ions was found to be 0.4066 mmol/g and 0.5502 mmol/g at 293 K and 303 K, respectively. Whereas in continuous flow fixed bed column, maximum adsorption capacity of PGP for Cu(II), Ni(II), Zn(II), Cd(II), and Cr(VI) ions was found to be 6, 2, 2, 2, and 0 mg/g, respectively. Kinetic study was carried out, and pseudo-first and pseudo-second-order models were tested. Pseudo-second-order models provided the best fit to experimental data. Thermodynamic study proved that the adsorption process was spontaneous and endothermic. Desorption experiments of copper were also carried out by the batch method using various solvents. Desorbed amounts, after shaking for 24 hours with for distilled water, 0.05 M acetic acid, 0.1 M acetic acid, 0.05 M HCl, 0.1 M HCl, 0.5 M NaCl, 1.0 M NaCl, and 0.1 M NaHCO_3 , were 0%, 29.5%, 36.3%, 77.3%, 79.5%, 2.1%, 6.4%, and 2.1%, respectively. These results proved that solution salinity did not affect the desorption process. Hence, adsorption is applicable from industrial wastewater containing other dissolved salts. Rao and Rehman [30] and Nembr [27] reported also that salinity solution did not affect adsorption experiments. Desorption study provided 79.5% of recovered copper ions using 0.1 M HCl solution [30] and 95% of recovered chromium ions using 0.1 N NaOH solution [28].

The adsorption of nickel onto modified PGP was studied by Bhatnagar and Minocha [31]. Pomegranate peels were first washed with double-distilled water and dried in an oven at $80 \pm 2^\circ\text{C}$ overnight. Dried peels were thermally activated at $600 \pm 5^\circ\text{C}$ for 1 hour in the presence of air, washed with distilled water to remove ash contents, and finally dried in an oven at $110 \pm 5^\circ\text{C}$ overnight. The obtained materials were sieved to particle size of 75–104 μm . Kinetic models analyzed were pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The pseudo-second-order described better adsorption of nickel ions on PPAC. Langmuir isotherm model fitted experimental data, and maximum adsorption capacity of PPAC for Nickel(II) ions was found to be 52.2 mg/g. Thermodynamic parameters suggested the endothermic and spontaneous nature of the adsorption process.

Ashraf et al. [32] investigated the use of PGP for lead ion removal. PGP was washed with 0.1 M HCl followed by

deionized water and dried in an oven at 60°C for 24 hours. The dried peels were crushed and employed for adsorption experiments. Isotherm study demonstrated that Freundlich model provided better fit to experimental data than Langmuir model. Lead uptake capacity of PGP was found to be 28.82 mg/g at pH 5 and temperature 22°C, with an initial metal concentration of 100 mg/l and adsorbent dose 2.5 g/L. The adsorption of lead onto PGP was studied by Alam and Nadeem [33], practically, in same operating conditions. PGP was washed with distilled water for three times and dried in open air then in oven at 65 ± 1°C. The dried peels were crushed and sieved to particle size 0.255 mm. The obtained materials were treated with 500 ml of 0.1 N solutions of HCl for 24 hours at 120 rpm and 30°C, washed by distilled water and dried. Maximum adsorption capacity for lead removal was found to be 113.25 mg/g at pH 4.5 and temperature 30°C, with an initial metal concentration of 400 mg/l and adsorbent dose 1 g/L. For initial metal concentration of 100 mg/L, maximum adsorption capacity was found about 80 mg/g, which is significantly higher than that obtained by Ashraf et al. [32]. This dissimilarity may be explained by the difference of pomegranate origin. Further treatments were studied by Alam and Nadeem [33] with H₂SO₄ and H₃PO₄ solution. Langmuir maximum adsorption capacity of lead ion removal was found to be 121.23 mg/g and 105.26 mg/g for PGP treated with H₂SO₄ and with H₃PO₄, respectively. Moreover, Alam and Nadeem [33] reported that the adsorption capacity of PGP decreased by increasing adsorbent dosage from 1 to 5 g/L, which was noted by other authors [27, 28].

Pomegranate peel was found to be a promising low-cost biosorbent for lead removal notably in its raw form [18, 32, 33]. Ay et al. [21] investigated the use, also, of raw PGP for lead removal. The peels were extensively washed with deionized water, crushed, further washed with deionized water to remove soluble materials, dried at 80°C for 48 hours, and sieved to particle size of 150 μm. After characterization of the biosorbent, isothermic, kinetic, and thermodynamic studies were carried out. Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models were analyzed. Langmuir model provided the best fit to adsorption data. The Langmuir maximum biosorption capacity of PGP for lead (II) ions found was 166.63 mg/g at 293 K and 193.94 mg/g at 323 K and pH 5.5. In kinetic study, the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models were employed. It was reported that lead biosorption follows to the pseudo-second-order kinetic model at whole time intervals. Thermodynamic study parameters proved an endothermic and spontaneous process. Similar kinetic and isotherm biosorption results were found by El-Ashtoukhy et al. [18] and Alam and Nadeem [33]. Whereas Ashraf [32] concluded from isotherm study that Freundlich model provided the best fit to experimental data.

Thapa and Pokhrel [34] studied the adsorption of arsenic (III) onto Fe (III)-loaded charred pomegranate waste (Fe-CPW). Raw pomegranate peel (RPW) was washed, dried in sunlight for a week, and powdered in a grain crusher. They were again dried in sunlight for about 3 days and sieved to

particle size of 212 μm. RPW was then treated with concentrated sulfuric acid (1 : 2, W/V ratio). The mixture was soaked for 24 hours at room temperature. Then, it was washed with distilled water until the pH was neutral, filtered and dried at 100°C for 6 hours in an air oven, and crushed and sieved to particle size 212 μm. The obtained adsorbent is named CPW and was mixed with 500 mL of 1.5 × 10⁻² M anhydrous ferric chloride solution at pH 3 and stirred for 24 hours. Then, it was filtered and washed with distilled water until the pH of the filtrate was neutral and finally dried for 24 hours at 100°C. It was sieved to a particle size of 212 μm. This material was named Fe-CPW and was used for removal of arsenic (III) ions. The optimum conditions for maximum arsenic removal were pH 9 and adsorbent dose over 45 mg/L, and equilibrium time found was 120 min. Maximum adsorption capacity of Fe-CPW was found to be 50 mg/g for As (III) ions removal at 298 K. Kinetic and thermodynamic studies have not been made.

Moghadam et al. [23] tested the pomegranate peel as potentially low-cost biosorbent for the ion (II) removal from aqueous solution. Peels were first washed with double-distilled water, dried in an oven at 70°C overnight, and crushed. It was then thermally activated at 500°C for 1 hour in the absence of air, washed with 0.1 M HCl solution and distilled water to remove ash contents, and finally dried in an oven at 90°C overnight. The material was sieved to particle size of 75 to 104 μm and was kept in a desiccator for further use. Kinetic models analyzed were pseudo-first-order and pseudo-second-order models. The pseudo-first-order model described better adsorption of iron (II) ions on activated pomegranate peel. Langmuir and Freundlich isotherm models were studied, and it was found that Freundlich fitted better experimental data. Maximum adsorption capacity of pomegranate peel activated carbon for Iron (II) ions was found to be 18.52 mg/g at optimum pH value 6 and adsorbent dose 1 g/L. Equilibrium time was found to be 40 min. Thermodynamic parameters suggested exothermic and spontaneous nature of the adsorption process.

Khawaja et al. [35] investigated the use of activated pomegranate peel to remove nickel (II) ions from water. The peels were washed and sun dried for 48 hours. The dried PGP was placed on a medium flame for 10 hours. After cooling, the obtained charcoal was crushed to particle size of 0.6 mm. Then, it was soaked for twenty-four hours in a solution mixture concentrated hydrochloric acid in a ratio of 1 : 4. The mixture was filtered, and the residue was washed with distilled water to remove the residual acid completely. The activated carbon obtained was dried at 110°C for 2 hours. Adsorption experiments were carried out in batch for metal concentration in a range 10–150 mg/L with a contact time of 60 minutes. The solution pH values studied were in a range of 3–11. Biosorbent doses used were 2, 5, 10, and 15 g/L. The optimum adsorption conditions were found to be biosorbent dose of 10 g/L, pH 7, and equilibrium time of 50 min. Adsorption isotherm study was carried out using Langmuir and Freundlich models. Both models fitted very well the experimental data. Maximum Langmuir adsorption capacity of PPAC for Nickel(II) was found to be 10.82 mg/g. Formaldehyde-modified PGP (FMPGP) had been used by

Najim and Yassin [27] for chromium (VI) ion removal. Yet, the same procedure of biosorbent preparation, as described above, was employed by Kumar and Kumar [36] for cadmium (II) ion removal. Adsorption experiments were performed at different initial pH values [2–10]. Maximum chromium uptake occurred at pH 6–8. Furthermore, it was reported that PGHC surface is positively charged up to pH 6, negatively charged in the pH range 6.8, and at pH 8.3 precipitation of cadmium started. The adsorption contact time was studied in a range of 0–200 min, and the equilibrium time was found to be about 120 min. The effect of adsorbent dose was studied from 0.5 to 3 g/L, and optimum adsorbent dose was 2 g/L. It was demonstrated also that temperature increase enhanced metal removal that may be related to an endothermic adsorption process nature. Isotherm, kinetic, and thermodynamic studies were carried out. Langmuir and Freundlich isotherm models were analyzed. Langmuir model was found to describe better adsorption data. Maximum Langmuir adsorption capacity of FMPGP for cadmium was found to be 18.52 mg/g at 303 K. Adsorption kinetics data were modeled using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The pseudo-second-order model gave the best data fit. Thermodynamic study confirmed the spontaneous and endothermic nature of cadmium adsorption onto FMPGP.

Turkmen et al. [37] tested the effect of microwave treatment on pomegranate peel adsorption efficiency to remove zinc (II) ions. Pomegranate peels were washed with distilled water to remove dusts and dried overnight at 70°C. It was granulated and then sieved through a 20 mesh sieve. Dry pomegranate peel was exposed to a maximum power of 800 W with an operating microwave frequency of 2.45 GHz (wavelength 12.2 cm) for 1 to 4 minutes. It was then added into ZnCl₂ solution (weight ratio = 1:3) and stirred at 500 rpm for 2 hours. Mixture was decanted, and the solid was soaked with HCl solution for 1 hour and then rinsed with deionized distilled water several times until pH 5.5. Modified PGP was dried overnight at 105°C. Dry pomegranate peels without microwave pretreatment was exposed to same chemical activation. It was used as a reference material. For the adsorption experiments, 0.25 g of the PGP activated carbon was mixed with 40 ppm of Zn solutions (50 ml). The mixture was stirred at 500 rpm for 2 hours at room temperature (22 ± 0.5°C). The adsorption capacities of activated carbon obtained by exposure microwave energy at different times were investigated. Remaining Zn (II) in solution was compared for pomegranate peels with and without microwave pretreatment. It was reported that removal efficiency of Zn (II) increased with the increasing microwave exposure time. Equilibrium adsorption capacity was found to be 6.78 mg/g for PGP without microwave pretreatment and 6.85 mg/g and 7.04 mg/g for microwave-activated PGP exposed for 1 and 4 minutes, respectively. Isotherm, kinetic, and thermodynamic studies had not been done.

Saeed et al. [38] studied the effect of chemical treatment on raw pomegranate peel for copper (II) adsorption in terms of % removal efficiency, any isotherms, kinetics, or thermodynamic study done. Quantitative adsorption capacity

had not been presented. The pomegranate peels were washed with distilled water and dried in open air then in a dryer at 333 K. The dried PGP was carbonized for 4 hours at 873 K. Physical activated PGP was divided into three parts. The first part was used without further treatment and named raw. The second part was soaked in the solution prepared from 1:1 ratio of heterogeneous mixture of zinc chloride and phosphoric acid and named CP-1. The third part was soaked in 0.1 M nitric acid for 24 hours and named CP-2. The adsorption experiments were carried out for initial metal concentration of 50 ppm of different metal ions (Cr (VI), Cu (II), Ni (II), Co (II), and Cd (II)). Particle size of adsorbent materials was in a range of 0.26–0.3 μm. The adsorption efficiency (%) versus time was presented. It was observed that CP-1 provided the best adsorption efficiency for metal removed followed by CP-2, while physical activated PGP without chemical treatment is less efficient for metal removal. For Cu (II), the adsorption capacity with material that named raw was 99.57%, 99.7% with PC-2, and 99.82% with PC-1.

Ben-Ali et al. [17] investigated the use of nonmodified PGP (raw) for copper removal. Pomegranate peel (PGP) was initially washed with preheated double-distilled water, several times. Then, it was dried in an air oven at 323 K overnight, crushed, and sieved to particle size in a range of 0–3.2 mm. Operating parameters studied were the initial metal concentration, the pH of the solution, the particle size, the temperature, and the contact time. The highest Cu(II) adsorption capacity is obtained at pH = 5.8, for a particle size of 630 μm, a temperature of 313 K, and a contact time of 2 hours and by increasing the initial concentration of Cu(II) solution. Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm models were used. Freundlich model did not fit the data. Experimental data were fitted to pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich kinetics models. The pseudo-second-order model gave the best fit. Thermodynamic analysis has indicated a spontaneous endothermic adsorption of Cu(II) on raw pomegranate peel. Maximum adsorption capacity of raw PP for copper removal was found to be 20.492 at 303 K and 30.12 mg/g at 313 K. From the most reported studies on PGP adsorbent, it was found that the adsorption capacity increases when the initial metal concentration increases until it reaches a constant value where no more metal ion could be removed. Increasing of adsorption capacity is due to the high quantity of metal ions in the concentrated solution. Furthermore, an increase in contact time resulted in an increase in adsorption. In most cases of metal ion adsorption, diffusion mechanism occurred in two stages. During the first stage, a rapid metal uptake occurred involving external and internal diffusion followed by a subsequent slow uptake in the second stage. The rate of adsorption is initially rapid, thanks to the full availability of exposed sites on the adsorbent. Then, it becomes slower due to repulsive forces between cations already set and the free ones in solution, which inhibit their access and increases the mass transfer resistance. The adsorption mechanism is highly influenced by the pH value of the metal aqueous solution. The pH range of 2–10 is generally chosen to study the effect of pH on

adsorption process. The effect of pH could be explained by considering the point of zero charge of the adsorbent (pH_{pzc}). The adsorbent surface is positively charged for $pH < pH_{pzc}$ and it becomes negatively charged at pH value above pH_{pzc} . Therefore, for pH values $< pH_{pzc}$, the adsorption is unfavorable because of repulsive electrostatic interactions between metal cations and positively charged functional groups. The maximum adsorption of metal occurs at pH above pH_{pzc} value when the adsorbent surface is negatively highly charged. From the reported study, the optimum pH range is 5–7 where adsorption is the only process responsible for the removal of metal since ions could be withdrawn by precipitation for a higher pH value. However, Thapa and Pokhrel [34] reported different results for arsenic removal. It was found that at pH 8, As(III) presents in solution as undissociated H_3AsO_3 . At pH 9, the predominant monoionic H_3AsO_3 and neutral H_3AsO_3 species are considered to be responsible for adsorption of As(III) by substitution of the hydroxyl ions or water molecules. Thus, the optimum pH for As(III) adsorption on Fe(III)-loaded activated pomegranate was found to be 9. Furthermore, the adsorption of chromium ions Cr_2O_2 was favorable at pH lower than pH 4 [27, 28]. In almost all studies, the increase of adsorbent dose increased the heavy metal removal efficiency (%), whereas it decreased adsorption capacity (mg/g). Furthermore, an increase in heavy metal uptake was also observed with the particle size decrease. It was also reported that temperature increase involved an enhancement of adsorption capacity; this can be explained by an increase in the ion mobility indicating the endothermic process nature. Although Moghadam et al. [23] found that iron adsorption on PGP-activated carbon was unfavorable when temperature increases indicating the exothermic process nature. Rao and Rehman [30] and Nembr [28] reported that salinity solution did not affect adsorption and desorption experiments. Hence, adsorption is applicable from industrial wastewater containing other dissolved salts. It was demonstrated that biosorbent could be regenerated. Desorption experiments were carried out using 0.1 N NaOH [28] and 0.1 M HCl [30] for chromium and copper recovery with efficiencies of 95% and 79.5%, respectively.

The literature results showed that isotherm adsorption data of studied metal were well described by Langmuir model [39]. Besides, El-Ashtoukhy et al. [18] and Rao and Rehman [30] reported that Freundlich model fitted better adsorption data of copper removal. Kinetic studies revealed that the pseudo-second-order model fitted the data with a very high regression coefficient ($R^2 \approx 1$). However, Moghadam et al. [23] demonstrated that data of iron (II) adsorption fitted the pseudo-first-order kinetic model. Furthermore, their results of thermodynamic studies showed an exothermic nature of iron (II) adsorption on activated PGP, while the endothermic process was reported for all other metal adsorption.

4.2. Dye Removal Applications. Pomegranate peel ability for dye removal was studied for the first time by Amin [40] for blue-106 dye removal. The procedure for preparing the

biosorbent was the same as that used by El-Ashtoukhy et al. [18] for metal removal, and it has been described above. Whereas activated carbon named AC1, AC2, and AC3 in El-Ashtoukhy et al.'s [18] study was named PC1, PC2, and PC3 in Amin's [40] study. A_{min} [40] showed that activated carbon prepared from chemically treated pomegranate peel is an effective adsorbent for removal of direct blue dye from aqueous solution. Removal of direct blue dye is pH dependent, and the maximum removal was attained at pH 2. The equilibrium adsorption is practically achieved in 120 min. It was also a function of adsorbate concentration and temperature of the solution. Adsorption equilibrium data follow Langmuir, Freundlich, and Temkin isotherm models. However, Langmuir model gave the best fit. Kinetic study of direct blue dye on PGP-activated carbons was performed based on pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion equations. The adsorption kinetics follows the pseudo-second-order model with intraparticle diffusion as one of the rate-determining steps. Thermodynamic parameters indicated the spontaneous and exothermic nature of the adsorption process. Maximum adsorption capacity was found to be 58.14 mg/g for PC3 at 298 K. In addition to their study of lead adsorption on PGP, Ay et al. [21] tested the biosorbent prepared as described above in metal removal section for Acid Blue AB40 removal. Optimum adsorption conditions were found to be 120 min for contact time, temperature of 20°C, pH 1.5, and adsorbent dose of 2 g/L. Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models were analyzed. Langmuir model provided the best fit to adsorption data. The Langmuir maximum biosorption capacity of PP for Acid Blue AB40 was 125.93 mg/g at 293 K and 138.1 mg/g at 323 K for pH 1.5. In kinetic study, the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models were employed. It was reported that Acid Blue AB40 biosorption follows the pseudo-second-order kinetic model at whole time intervals. Thermodynamic study parameters proved an endothermic and spontaneous process.

Güzel et al. [24] studied the adsorption of methylene blue onto raw PGP. Pomegranate peels were firstly washed with distilled water, dried at 70°C for 24 hours, and crushed and sieved to particle size of 500 μ m. No other physical or chemical treatments were given prior to adsorption experiments. Adsorption conditions such as adsorbent dose of 0.1–1.0 g/L, pH 2–12, contact time 0–400 min, initial dye concentration 25–300 mg/L, and ionic strength were studied. Equilibrium time was found to be 150 min, optimal pH value was 7, and adsorbent dose of 2 g/L. Maximum adsorption capacity of raw PP for methylene blue was found to be 36.36 mg/g at 303 K, 28.74 mg/g at 313 K, and 26.67 mg/g at 323 K. Adsorption kinetics data were modeled using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Adsorption isotherm used for fitting experimental data was Langmuir and Freundlich models. The results indicated that the pseudo-second-order model gave the best fit to kinetic data. Langmuir model fitted isotherm adsorption data better than Freundlich model. Thermodynamic study indicated that adsorption process was physical, exothermic, and spontaneous. Desorption experiments to

recover the MB were conducted using different desorbent agents (H_2O , HCl , HNO_3 , H_3PO_4 , CH_3COOH , and citric acid). It was reported that citric acid provided the highest desorption percentage. The effects of salt solutions on MB adsorption were discussed. Results showed that MB removal efficiency decreased from 21.67% to 3.96% with an increase in NaCl concentration from 0 mol/L to 1.0 mol/L. This indicated that salt solutions disadvantaged MB adsorption on PGP.

The adsorption of amaranth dye from aqueous solution using PGP activated carbon was studied by Ali et al. [41]. The activation process was performed by chemical treatment. Pomegranate peels were washed with double-distilled water and dried in an oven at 70°C for 24 hours. The dried pomegranate peels were crushed, soaked with distilled water for two hours at boiling point, and filtered finally. This process was repeated to remove all colored and soluble materials. The dried PGP was mixed with a volume of concentrated H_2SO_4 at room temperature for two hours. The excess of the acid was removed by washing the solid residue with distilled water and the material was dried at room temperature. The activated carbon prepared was kept in an air oven at 110°C for 8 hours and then was crushed to a fine powder material. Adsorption experiments were carried out in batches. Experimental parameters such as pH, contact time, adsorbent dose, and temperature were studied. The optimum conditions found were contact time of 25 min, pH 3, and adsorbent dose of 0.25 g/L. Pseudo-first-order and pseudo-second-order kinetic models were used to analyze adsorption data. Isotherm study was carried out using Langmuir and Freundlich models. Experimental data fitted pseudo-second-order kinetic model and Langmuir adsorption model. The maximum Langmuir adsorption capacity for activated PGP was found to be 3.448 mg/g. Thermodynamic parameters indicated that the adsorption of amaranth dye onto activated PGP was an endothermic process.

Remazol brilliant blue reactive (RBBR) dye adsorption using pomegranate peel-activated carbon (PPAC) prepared by microwave-induced KOH activation was analyzed by Ahmad et al. [16]. Pomegranate peel was washed thoroughly with distilled water to remove adhering dirt particles from the surface. PGP was dried in an oven at 70°C and crushed and sieved to a particle size of 1-2 mm. The carbonization process was carried out at temperature of 700°C for 30 min under purified N_2 flow. The produced material was mixed with KOH at different impregnation ratios (IR) and was modified with the microwave oven with a frequency of 2.45 GHz. The activated carbon (PPAC) was washed sequentially with 0.1 M hydrochloric acid and then with water. Kinetics of RBBR dye adsorption was analyzed with pseudo-first-order model, pseudo-second-order model and Avrami and Elovich models. It was found that data follow pseudo-second-order model. Adsorption isotherm models studied were Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Sips, Vieth-Sladek, Brouers-Sotolongo, and Radke-Prausnitz. It was demonstrated that Freundlich model provided the best fit to experimental data. Maximum Langmuir adsorption capacity of PPAC for

RBBR dye was found to be 370.86 mg/g at 303 K. BET surface area and total pore volume for PPAC were found to be $941.02 \text{ m}^2/\text{g}$ and $0.47 \text{ cm}^3/\text{g}$, respectively.

Zarroug et al. [42] tested various treatment conditions (carbonization time and temperature) on physical PGP properties. Pomegranate peels were washed with distilled water, dried, crushed, and sieved. Then, it was impregnated with phosphoric acid (50%) 4:1 (w/v) at a boiling temperature for 2 hours. The chemical activated carbon was dried at room temperature. Then, it was heated in a steam of nitrogen saturated with water vapor to a final heat treatment temperature of 300°C , 400°C , and 500°C and kept at this temperature for 2, 3, and 4 hours. The water vapor fraction was fixed to 12.18%. After being cooled, all prepared carbons were washed several times with hot water until the filtrate pH became higher than 6. The washed samples were dried at 110°C to obtain the final product. It was reported that the BET surface area of the PGP-activated carbon depended on temperature and treatment time and reached $1819 \text{ m}^2/\text{g}$ after thermal treatment at 300°C for 2 hours. Textural properties such as BET surface area, pore volume, micropore volume, mesopore volume, and pore diameter of the obtained activated carbon were presented. Maximum adsorption capacity of PPAC for Methylene blue was found to be 345 mg/g.

Radaei et al. [43] investigated the use of PGP activated carbon for reactive blue 19 (RB19) removal. Pomegranate peels were dried in an oven for 2 hours at 100°C until a constant weight was reached and were then crushed. They were soaked for 24 hours with 50 wt% phosphoric acid in the ratio of 1:1 (w/v) at room temperature. The obtained product was filtered and dried for 1 hour at 500°C . It was washed sequentially several times with hot distilled water, until pH of the washing solution became neutral. Finally, the PGP activated carbon (AC) was powdered and sieved. The BET method showed that the average surface of the obtained PGP activated carbon was $825.46 \text{ m}^2/\text{g}$. Response surface methodology was applied as an experimental design to explore the optimal adsorption conditions (initial pH, adsorbent dose, dye concentration, and contact time) of PGP AC for RB19 dye removal from aqueous solutions. Optimum conditions were found to be pH 11, adsorbent dose of 1.025 g/L, initial dye concentration of 100 mg/L and contact time of 6.8 min. The average dye removal efficiency was found to be 98.7%. This value was close to the model prediction of 98.1%.

4.3. Miscellaneous Applications. Bhatnagar and Minocha [44] investigated the use of thermally activated PGP as adsorbent for 2,4-dichlorophenol. Pomegranate peels were washed with double-distilled water, dried in an oven at $80 \pm 2^\circ\text{C}$ overnight, and crushed to the particle size of $75\text{--}104 \mu\text{m}$. They were then thermally activated at $600 \pm 5^\circ\text{C}$ for 1 hour in the presence of air. After activation, the ash content was removed by washing it with distilled water and dried in an oven at $110 \pm 5^\circ\text{C}$ overnight. Adsorption experiments were carried out in the batch column process. The effect of contact time from 0 to 600 min and initial dye concentration from 3.5×10^{-4} to 6.5×10^{-4} M were studied.

Initial pH was chosen in a range of 5.5–6.5 and adsorbent dose of 10 g/L. Equilibrium time was found to be 540 min. Adsorption kinetics data were modeled using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The results indicated that the pseudo-first-order model gave the best fit to kinetic data. Langmuir isotherm model was used for fitting experimental data. Maximum Langmuir adsorption capacity of PGP activated carbon for 2,4-dichlorophenol was found to be 75.8 mg/g and 96.2 mg/g at 298 K and 318 K, respectively. Thermodynamic study indicated that the adsorption process was endothermic and spontaneous. Column adsorption was studied with a glass column (50 cm × 1.05 cm) loaded with PGP-activated carbon. Double-distilled water was used to rinse the adsorbent and to remove any bubbles present. 2,4-dichlorophenol solution was passed through the column at a flow rate of 2.5 mL/min. At the column outlet, effluent samples of 10 mL were taken, and the concentration of 2,4-dichlorophenol was determined by UV-VIS. This process has continued until the concentration in the column effluent became constant and reached nearly 90% of the influent concentration ($C/C_0 \approx 0.9$). Rouabeh and Amrani [26] studied the adsorption of NO_3^- from aqueous solution using PGP activated carbon. Pomegranate peels were washed with distilled water, dried in an oven for two hours at 105°C, and crushed and sieved to particle size in a range of 0.3–0.6 mm. The obtained materials were divided into two parts; the first one was carbonized for one hour at 500°C and was named AC. The second part was soaked for 24 hours in a mixture of phosphoric acid 1 M and zinc chloride 1 M in a ratio of 1:1 (V/V), dried, and carbonized as mentioned above. The activated carbon obtained was then neutralized with 1% NaHCO_3 solution, extensively washed with deionized water, and dried at 90°C. It was named AC1. AC and AC1 were characterized and compared. Adsorption experiments were carried out using AC1. The effects of the adsorption contact time (0–200 min) and pH (2–11) were studied. The equilibrium time was found to be 45 min, and maximum removal was reached for pH 7.5–8.5. Adsorption isotherm models used were Langmuir and Freundlich. The Langmuir model fits better adsorption data. Maximum Langmuir adsorption capacity of PPAC for nitrate was found to be 78.125 mg/g. Adsorption kinetics data were modeled using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The results indicated that the second-order model provided the best fit to adsorption kinetic data, and the intraparticle diffusion model had an insignificant role at the initial stage of the adsorption process. Adsorption capacity of modified PGP for phenol removal was evaluated by Zarroug et al. [42]. The biosorbent was prepared as described in Section 3.1. The maximum adsorption capacities for three (time and temperature) activation conditions used, (2 h, 300 K), (3.5 h, 350 K), and (3 h, 400 K), were found to be 109 mg/g, 96 mg/g, and 103 mg/g, respectively. The adsorption process achieved the equilibrium at 150 min. Najafpoor et al. [45] also studied the phenol adsorption on PGP-activated carbon. Pomegranate peels were washed with distilled water to remove impurities and then dried at 105°C for 24 hours. The dried pomegranate peels were carbonized at 500°C for 2 hours and

then crushed to particle size of 0.074 mm–0.250 mm. The effects of contact time (0–210 min), pH (2–12), adsorbent dose (0.1–0.7 g/L), and initial phenol concentration (10–100 mg/L) was studied. The optimum adsorption conditions were pH=7 and adsorbent dose of 0.6 g/l. Equilibrium time found was 120 min. Langmuir and Freundlich isotherm models were analyzed. Freundlich model gave better fit to the experimental data. Maximum Langmuir adsorption capacity of PPAC for phenol was found to be 344.86 mg/g. The most significant study related to the use of PGP biosorbent for the removal of pollutants from aqueous solution is presented in Tables 2 and 3. Table 2 synthesizes experimental adsorption conditions as well as activation treatment employed in the literature for pollutant removal using raw and activated pomegranate peels. Table 3 summarizes the main results obtained for maximum adsorption capacity, isotherm, kinetic, and thermodynamic studies. PGP-activated carbon was shown to be a promising biosorbent for removal of metal, dye, and organic pollutants from aqueous solutions with high adsorption capacities compared to other agriculture by-products (Table 4). The advantage of using agricultural by-products chiefly as raw materials for wastewater treatment is that these materials are renewable and environmentally friendly biosorbent.

5. Physical and Chemical Properties of PGP-Activated Carbon

Raw pomegranate peels constitute a low-cost biosorbent that is very efficient and showed a high adsorption capacity towards metal, dye, and organic pollutant removal. Their physical and chemical properties described in Section 2 can be improved by activation treatment. This allowed the increase of specific surface area, development of pore size, and volume distribution. The modification with chemical compounds was frequently employed to increase the adsorption capacity of material. Chemical agents generally used were acids (H_2SO_4 , HNO_3 , HCl , CH_3COOH , H_3PO_4 , and formic acid), bases (KOH , NaOH , NaHCO_3 , and $\text{Ca}(\text{OH})_2$), oxidizing agents (H_2O_2 and K_2MnO_4), and other chemical compounds such as the formaldehyde and zinc chloride. Results of physical properties of PGP-activated carbons showed that the carbon content increased significantly up to 80% while the other elements decreased such as hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S). Furthermore, the moisture and volatile content also decreased significantly; this was explained by the water loss and the decomposition of volatile compounds notably during thermal treatment. The surface morphology changed considerably after chemical or physical treatment. It became more rough and uneven. The scanning electron microscopy image showed a significant pore development and an increase of porosity and surface area as shown in Figure 8. Nevertheless, we found a greater pore development of a well-washed pomegranate peel (Figures 4(e) and 4(f)). Our results disclose a good opportunity for PGP low-cost biosorbent that does not require chemical or/and physical activation. Activation parameters such as temperature, chemical agent, and treatment time modified

TABLE 2: Biosorption operating conditions of different pollutants from the literature by pomegranate peel biosorbent.

	Adsorbate	Q_m (mg/g)	Isotherm study	Kinetic study	Thermo dynamic study	ΔH (kJ/mol)	ΔS (J/mol.K)	References	
1	Blue dye-106	PC1	Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Harkins-Jura	Pseudo-second-order, intraparticle diffusion, Elovich, pseudo-first-order	Spontaneous and exothermic	-9.90	-25.7	[40]	
		PC2				54.05	-1.24		-31.823
		PC3				58.14	-13.24		-33.395
2	Lead (II)	AC1	Langmuir, Temkin, Freundlich	Pseudo-first, pseudo-second-order, Elovich, intraparticle diffusion	Not studied	13.986		[18]	
		AC2				17.637			
		AC3				17.953			
		Raw				13.870			
3	Copper (II)	AC1	Freundlich, Temkin, Langmuir	Pseudo-first, pseudo-second-order, Elovich, intraparticle diffusion	Not studied	18.050		[18]	
		AC2				19.193			
		AC3				21.978			
		Raw				1.3185			
3	Chromium (VI)	MPPGP	Langmuir, Dubinin-Radushkevich, Freundlich, Tempin models	Langmuir, Dubinin-Radushkevich, Freundlich, Temkin models	Not studied	47.17		[27]	
		FMPGP				49.75			
4	Cadmium (II)	FMPGP	Langmuir, Freundlich	Pseudo-first-order, intraparticle diffusion	Spontaneous and endothermic	19.77	69.15	[36]	
5	Remazol blue	PPAC	Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Sips, Vieth-Sladek, Brouers-Sotolongo Radke-Prausnitz	Pseudo-first-order, pseudo-second-order, Avrami, and Elovich	Spontaneous and endothermic	30.88	54.46	[16]	
6	2,4-dichlorophenol	PPAC at 298	Langmuir	Pseudo-first-order, pseudo-second-order, intraparticle diffusion	Spontaneous and endothermic	75.8		[44]	
		PPAC at 318				96.2			
		Raw at 303K				36.36			
7	Methylene blue	Raw at 313K	Langmuir, Freundlich	Pseudo-first-order, pseudo-second-order, intraparticle diffusion	Spontaneous and exothermic	28.74	-11.87	[24]	
		Raw at 323K				26.67			
8	Nickel (II)	PPAC	Langmuir	Pseudo-first-order, pseudo-second-order, intraparticle diffusion models	Spontaneous and endothermic	8.6	144.2	[31]	
9	Copper (II)	Raw at 313K	Langmuir isotherm; Freundlich isotherm Temkin isotherm, Dubinin-Radushkevich	Pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion	Spontaneous and endothermic	67.196	239	[17]	
10	As (III)	Fe-CPW	Langmuir, Freundlich	Not studied	Not studied			[34]	

TABLE 2: Continued.

	Adsorbate	Q_m (mg/g)	Isotherm study	Kinetic study	Thermo dynamic study	ΔH (kJ/mol)	ΔS (J/mol.K)	References
11	Copper (II)	Raw at 293K Raw at 303K	0.40661 0.55021	Langmuir, Freundlich	Pseudo-first-order, pseudo-second-order	Spontaneous and endothermic	25.84 113.8	[30]
12	Amaranth dye	PPAC	3.448	Langmuir, Freundlich	Pseudo-first-order, pseudo-second-order	Spontaneous and endothermic	23.75 29.25	[41]
13	Iron (II)	PPAC	18.52	Langmuir, Freundlich	Pseudo-first-order, pseudo-second-order	Spontaneous and endothermic	-1.08354 -1.48	[23]
14	Chromium (VI)	PGHC	35.2	Langmuir (1, 2, 3, 4), Freundlich, Temkin, Dubinin-Radushkevich	Pseudo-first-order, pseudo-second-order, Elovich, intraparticle diffusion	Not studied		[28]
15	Nickel (II) Cobalt (II)	Raw Raw	7.54 8.98	Langmuir, Freundlich	Not studied	Spontaneous and endothermic	31.244 38.548 115.148 148.541	[29]
16	Lead (II)	Raw	166.63	Langmuir, Freundlich, Dubinin-Radushkevich	The Lagergren first-order, pseudo-second-order, Elovich kinetic, intraparticle diffusion	Spontaneous and endothermic	4.43 108.04	[21]
17	Acid blue 40	Raw	125.93	Langmuir, Freundlich, Dubinin-Radushkevich	The Lagergren first-order, pseudo-second-order, Elovich kinetic, intraparticle diffusion	Spontaneous and endothermic	22.04 158.81	[21]
18	Lead (II)	HCL H ₂ SO ₄ H ₃ PO ₄ Native	113.25 121.23 105.26 111.52	Langmuir, Freundlich	Pseudo-first-order, pseudo-second-order	Not studied		[33]
19	Nitrate	AC1	78.125	Langmuir, Freundlich	Pseudo-first-order, pseudo-second-order, intraparticle diffusion	Not studied		[26]

TABLE 3: Biosorption results of different pollutants from the literature by pomegranate peel biosorbent.

	Adsorbate	Treatment	Process variables					References	
			Contact time (min)	Initial concentration (mg/L)	T (°C)	pH	Adsorbent dosage (g/L)		
1	Blue dye-106	PC1	Carbonized for 1 hr 500°C in the absence of air	180	20	25	2	2.5	[40]
		PC2	Sample was soaked for 24 h in a mixture of phosphoric acid and zinc chloride (50wt%) at a ratio 1 : 1 and then carbonized as PC1	180	20	25	2	2.5	
		PC3	Sample was soaked for 24 h in a nitric acid solution (10wt. %) and then carbonized as PC1	180	20	25	2	2.5	

TABLE 3: Continued.

Adsorbate		Treatment	Process variables				References		
			Contact time (min)	Initial concentration (mg/L)	T (°C)	pH		Adsorbent dosage (g/L)	
2	Lead (II)	AC1	Carbonized 1 h at 500°C Sample was soaked for 24 h in phosphoric acid and zinc chloride in a ratio of 1 : 1 and carbonized as AC1	180	20	25	5.8	2.5	[18]
		AC2		180	50	25	5.8	2.5	
	Copper (II)	AC3		180	50	25	5.8	2.5	
3	Chromium (VI)	FMPGP	Pomegranate peel reacted with 8% formaldehyde solution at a ratio 1 : 5w/v, at 60°C for 4 h	100	10	20	2	2	[27]
4	Cadmium (II)	FMPGP	Pomegranate peel reacted with 8% formaldehyde solution at a ratio 1 : 5 w/v, at 60°C for 4 h	200	10	30	6	2	[36]
5	Remazol blue	PPAC	Carbonized at 700°C for 30 min under purified N ₂ flow, mixed with KOH pellets, and activated microwave oven with a frequency of 2.45 GHz	1440	50	30	2	1	[16]
6	2,4-dichlorophenol	PPAC	Carbonized at 600 ± 5°C for 1 h in the presence of air	600	0.65 ¹	25	5.5	10	[44]
7	Methylene blue	Raw		300	25	30	7	2	[24]
8	Nickel (II)	PPAC	Carbonized at 600 ± 5°C for 1 h in the presence of air	480	0.45 ¹	25	5.5	10	[31]
9	Copper (II)	Raw		120	20	30	5.8	3	[17]
10	Arsenic (III)	Fe-CPW	Sample was soaked with concentrated sulfuric acid(1 : 2, W/ V ratio) for 24 hours at room temperature, 20 g of CPW was mixed with 500 mL of 1.5 × 10 ⁻² M anhydrous ferric chloride solution for 24 h		20	25	9	1	[34]
11	Copper (II)	Raw		1440	0.472 ¹	20	4.5	0.5	[30]
12	Amaranth dye	PPAC	Sample was soaked with concentrated H ₂ SO ₄ (2N) at room temperature for 2h	25	35	25	3	0.25	[41]
13	Iron (II)	PPAC	Carbonized at 500°C for 1h in the absence of air; the ash was removed by washing it with HCl solution (0.1 M) and distilled water	80	100	29	6	1	[23]
14	Chromium (VI)	PGHC	Sample was treated with a mixture of 98% H ₂ SO ₄ and 1% NaHCO ₃ solution	180	150	25	1	6	[28]
15	Nickel (II)	Raw		60	10	30	6	3	[16]
	Cobalt (II)	Raw		60	10	30	6	3	
16	Lead (II)	Raw		120	82.88	20	5.5	1	[21]
17	Acid Blue40	Raw		120	189.2	20	1.5	2	[21]
18	Lead (II)	HCL	Sample was treated with 0.1 N solution of HCl for 24 h at 30°C	1440	400	30	4.5	1	[33]
		H ₂ SO ₄	Sample was treated with 0.1 N solution of H ₂ SO ₄ for 24 h at 30°C						
		H ₃ PO ₄	Sample was treated with 0.1 N solution of H ₃ PO ₄ for 24 h at 30°C						
19	Nitrate	AC1	Chloride 1 M in a ratio of 1 : 1(V/V) for 24 h and then carbonized at 500°C for 1 h	200	100	25	7.2	2	[26]

TABLE 4: Langmuir constants q_{\max} (mg/g) of various untreated waste adsorbents for pollutant removal.

Natural adsorbent	Pollutant	q_{\max} (mg/g)	References
Cucumber peel	Lead (II)	133.60	[46]
Rice straw	Cobalt (II)	28.5	[47]
<i>L. domesticum</i> peel	Nickel (II)	10.1	[48]
Litchi pericarp	Copper (II)	8.83	[5]
Peanut hull	Copper (II)	21.25	[49]
Jackfruit peels	Methylene blue	285.73	[50]
Coffee husks	Copper (II)	7.496	[51]
Coffee husks	Cadmium (II)	6.854	[51]
Coffee husks	Zinc (II)	5.565	[51]
Coffee husks	Chromium (VI)	6.961	[51]
Yellow passion	Methylene blue	44.70	[52]
<i>Thuja orientalis</i>	Acid blue 40	97.06	[53]
Coir pith	Nickel (II)	15.95	[54]
Coir pith	Cobalt (II)	12.82	[54]
Coir pith	Chromium (VI)	11.56	[54]
<i>Pinus sylvestris</i>	Nickel (II)	3.12	[55]
Pomegranate peel	Copper (II)	30.12	[17]
Pomegranate peel	Lead (II)	166.63	[21]
Pomegranate peel	Acid blue 40	125.93	[21]
Pomegranate peel	Methylene blue	36.36	[24]
Pomegranate peel	Nickel (II)	7.54	[29]
Pomegranate peel	Cobalt (II)	8.98	[29]
Pomegranate peel	Chromium (VI)	47.17	[27]

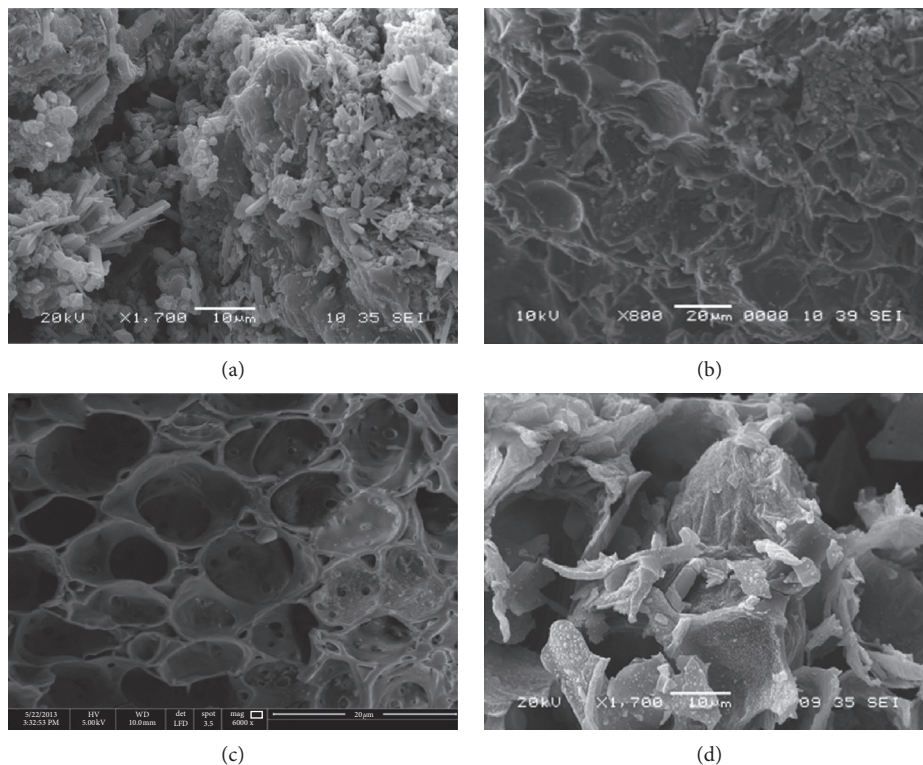


FIGURE 8: Scanning electron microscopy of physical- and chemical-activated PGP: (a) (PC2, AC2) [18, 40], (b) (AC1) [26], (c) (PPAC) [16], (d) (PC3, AC3) [18, 40].

differently the activated carbon morphology. Yet, the textural property of PGP-activated carbon prepared by phosphoric acid and thermal activation, as described above [43], was characterized by BET surface area of 825.46 m²/g,

pore volume of 0.3455 cm³/g, and pore diameter of 14.35 Å. BET surface area of PGP-activated carbon prepared by phosphoric acid and water vapor activation obtained for different activation conditions ranged between 880 and

1819 m²/g. Pore volumes obtained varied from 0.525 to 1.04 cm³/g with micropore and mesopore volumes of (0.447, 0.0782 cm³/g) and (0.983, 0.057 cm³/g), respectively. Pore diameters reported ranged between 20.70 and 24.96 Å [42].

6. Conclusion

The purpose of this work is to reveal, for the first time to our knowledge, pore development of raw pomegranate peel after tannin extraction (aqueous washing), furthermore, to consider the potential of PGP as low-cost biosorbent for wastewater treatment from a literature review. Physical and chemical properties of raw PGP are presented. Different biosorbent treatment procedures as precursors of activated carbon are presented. Experimental and optimum conditions during the adsorption process to remove whatever metal, dye, or organic pollutants are defined. Isotherm, kinetic, and thermodynamic PGP adsorption results are analyzed, and physical and chemical properties of PGP activated carbon are presented. It appears from this study, review, and experimental results that the activated carbon produced from pomegranate peels constitutes a promising biosorbent for water and gas purification. Nevertheless, the process energy and water consumption should be quantified. Indeed, a great quantity of water is generally employed to remove any residual reactants used for chemical activation such as nitric, sulfuric, or phosphoric acids especially for large-scale processes. The resulted wastewater contains a considerable amount of activation agents that induce environmental impacts. Furthermore, the energy consumed and gases produced during the pyrolysis of biosorbents activation increase the environmental impacts of the activated carbon production. Thus, recovery of chemical activation agents from washing water and gas recovery for use as an additional source of energy reduce environmental risks and improve activated the carbon production process. For additional savings, the life cycle assessment method could minimize environmental risks associated with PGP-activated carbon fabrication. Besides the environmental impacts assessment associated with activated carbon preparation, the regeneration of charged materials after adsorption is of crucial interest from an environmental and economical point of view. Contrariwise, raw pomegranate peel compared to activated carbon constitutes an eco-friendly biosorbent with high adsorption capacity of pollutants and with low environmental impacts. Indeed, during the biosorbent preparation, no activation or pyrolysis is needed. Moreover, washing water is used to recover tannins extracted from pomegranate peels. The recovered tannin is used as natural dyes or for adhesive fabrication in substitution of formaldehyde products.

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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