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Agro-Waste Derived Biomass Impregnated with TiO_2 as a Potential Adsorbent for Removal of As(III) from Water

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Abstract: A novel type of adsorbent, TiO_2 impregnated pomegranate peels (PP@TiO_2) was successfully synthesized and its efficacy was investigated based on the removal of As(III) from water. The adsorbent was characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectrometer (EDS), X-ray Diffraction (XRD) analysis, and Fourier Transform Infrared (FTIR) Spectroscopy, to evaluate its morphology, elemental analysis, crystallinity, and functional groups, respectively. Batch experiments were conducted on PP@TiO_2 for As(III) adsorption to assess the adsorption isotherm, effect of pH, and adsorption kinetics. Characterization data suggested that TiO_2 was successfully impregnated on the biomass substrate. The equilibrium data better fitted to the Langmuir isotherm model having a maximum adsorption capacity of 76.92 mg/g and better distribution coefficients (K_D) in the order of $\sim 10^3$ mL/g. The highest percentage of adsorption was found at neutral pH. The adsorption kinetics followed the pseudo-2nd-order model. X-ray Photoelectron Spectroscopy (XPS) of the adsorption product exhibited that arsenic was present as As(III) and partially oxidized to As(V). PP@TiO_2 can work effectively in the presence of coexisting anions and could be regenerated and reused. Overall, these findings suggested that the as-prepared PP@TiO_2 could provide a better and efficient alternative for the synergistic removal of As(III) from water.

Keywords: adsorption; TiO_2 ; As(III); photocatalytic oxidation; adsorption capacity; isotherm model

1. Introduction

Safe water is the basic need for the existence of life. Due to the rapid industrialization, the world's supply of safe water is decreasing and the pollutant levels are rising steadily [1–3]. Arsenic (As) contaminated water is one of the most challenging environmental concerns because of its chronic toxicity and carcinogenicity (black foot disease; skin, liver, bladder, kidney, and lung cancer; stillbirths; and heart attacks) [4]. Naturally occurring As-contaminated groundwater has caused hazardous effects to hundreds of millions of population globally, especially in Bangladesh, India, Pakistan,

China, Argentina, Cambodia, Chile, Mexico, New Zealand, Taiwan, Vietnam, the USA, and Nepal as well [5,6]. Arsenic is introduced into groundwater through natural sources such as volcanic emissions, geochemical activity, rock, and soil weathering as well as the anthropogenic sources such as mining activities, combustion of fossils fuel, agricultural chemicals, wood preservatives, acid mine drainage wastewater, and other industrial discharges of metal processing, semiconductor, copper smelting, electroplating, pigments, dyestuff, and paints [7–9]. Inorganic arsenic has been classified as a human carcinogenic substance of Group 1 by the International Agency for Research on Cancer (IARC) [5,10]. Based on its exposure concerns and acute lethal effects on human health, WHO and USEPA promulgated the maximum contamination limit (MCL) for arsenic in drinking water not to exceed 10 ppb (0.01 mg/L) [11,12]. However, some South Asian countries have followed MCL of 50 ppb (0.05 mg/L) as their drinking water standard [13–15].

Inorganic arsenic species are the most abundant in natural waters. The predominant species of toxic inorganic arsenic in waters are either arsenite (As(III)) or arsenate (As(V)). Under aerobic conditions, e.g., in oxygen-rich surface waters, As(V) is dominant. Under anaerobic conditions, e.g., in groundwater, the reduced As(III) dominates, which is more hazardous and more challenging to sequester from water by most conventionally applied techniques than As(V) [16–21]. Therefore, As(III) is generally sequestered by oxidizing it to As(V) followed by adsorption, ion exchange, coagulation-precipitation, or membrane separation processes [22–26]. In developing countries, adsorption is the best method compared to others because it is simple, cheap, and competent with minimal sludge generation and can be used in water having a trace level of contaminants [5,27]. The oxidation pretreatment can be achieved using chemical reagents (e.g., ozone, hydrogen peroxide, potassium permanganate, ferrous salt, or manganese oxide, etc.) [28], but this may result in a significant increase in treatment costs and cause secondary pollutants of residual reagents and by-products [29]. Recently, TiO₂ (the most common semiconductor photocatalyst) has been reported as an environment-friendly and cheap material in oxidizing As(III) to As(V) under visible and ultraviolet light irradiation [30–36]. During the photocatalytic oxidation of As(III), it is oxidized first into As(IV) with superoxide radicals produced at the TiO₂ surface and then further oxidized to As(V) by reaction with dioxygen, hydroxyl radicals, or a photogenerated hole [32–34]. Moreover, past studies have proposed TiO₂ as an adsorbent for the remediation arsenic from aqueous solution [36–41]. However, the low adsorption capacities as well as the difficulty of separation and recovery of the small particles from water usually limit the direct application of suspended TiO₂ particles in arsenic removal [32].

Like TiO₂, waste biomaterials can be utilized as attractive water treatment materials because of being cheap, widely available, non-toxic, and biodegradable. In the last decades, biomass-based adsorbents have been used for sequestration of arsenic from water. Some of these biomasses includes orange waste [20,21], watermelon rind [42], sugarcane bagasse [43,44], pomegranate waste [18], *Staphylococcus xylosus* [10] etc. Biomass usually is composed of cellulose, pectin, lignin as major constituents and provides multiple functional groups (e.g., –OH, –COOH, and C=O), which can efficiently bind arsenic through complexation and ion exchange. Though biomass has been used as adsorbents for removing pollutants, they have a less adsorptive capacity for As(III) in their raw form. Thus, effective sorbents for arsenic can be synthesized by combining TiO₂ and biomass. TiO₂ impregnated biomass offers the synergistic benefit of biomass and TiO₂, which can not only adsorb As(III) but also catalyze the oxidation of As(III) to As(V). Biomass can also support the dispersion of TiO₂ particles increasing the stability and recovery of tiny particles. Several interactions (e.g., H-bonding, electrostatic interaction, and C–Ti–O or C–O–Ti bonds) may be formed between biomass and TiO₂ [45]. A few works have been reported on using chitosan/TiO₂ composite for remediation of some toxic elements, such as Cd²⁺, Ni²⁺, Cu²⁺, Ag⁺, and Pb²⁺ from water [46–48]. Past studies have reported that carbon adsorbents derived from agricultural waste are more effective for the removal of heavy metals and antibiotics from water and wastewater [49–51]. Cruz et al. [52] conducted an adsorption experiment using agrowaste-derived biochars impregnated with ZnO for removing As(V) and Pb(II) from water. Recently, Pincus et al. [53] reported chitosan-TiO₂-Cu composite photocatalyst for the removal of Arsenic.

There are voluminous research works available in the literature regarding the use of agro-waste derived biomass materials [3,10,18,20,21,28,31,42,44] and bare nano-TiO₂ [37–40] for sequestration of heavy metals including arsenic from aqueous medium. However, impregnation of TiO₂ into agro-waste derived biomass is still lacking though TiO₂ composite with other precursors like activated carbon [32], metal oxides [36], chitosan [45–48], graphene [54], and carbon nanotube [55] have been studied. To the best of our knowledge, no reports are available in the literature on the synthesis of TiO₂ impregnated pomegranate peels (PP@TiO₂) for the removal and oxidation of As(III) simultaneously. Because of such circumstances, PP@TiO₂ is supposed to be a novel materials herein studied and its application as an adsorbent for removal of As(III) was proposed.

The objective of the present work was to fabricate TiO₂ impregnated pomegranate peels (PP@TiO₂) by using a modified sol-gel method and to investigate its adsorption behaviors of As(III) from water under different conditions through batch experiments. The adsorption characteristics of the PP@TiO₂ were analyzed by SEM, EDS, XRD, FTIR, and XPS. The adsorption isotherms, kinetics parameters, effect of pH, and effect of common coexisting anions on As(III) adsorption were also investigated and discussed. From the results, the plausible adsorption mechanisms had been proposed. A desorption study was conducted to investigate the regeneration and reusability of the adsorbent. With further development, this research may offer a cost-effective, environmentally friendly, and easy-handle treatment alternative for remediation of arsenic from aqueous medium.

2. Results and Discussion

2.1. Adsorbent Characterization

The surface morphology of adsorbent was studied through SEM measurements. The SEM images (Figure 1a,b) illustrate the porous nature and irregular morphology of cross-linked pomegranate peels powder (PP) and PP@TiO₂. The decrease in porosity in PP@TiO₂ (Figure 1b) as compared to PP (Figure 1a) is probably due to the occlusion of pores by TiO₂ particles. As shown, some particles of TiO₂ are attached to the surface of biomass. Therefore, it is justified that the impregnation of PP by TiO₂ has been done effectively. SEM image of As(III) adsorbed PP@TiO₂ (Figure 1c) shows that the surfaces of adsorbent are covered because of the adsorption of arsenic and forms layer on the surfaces. EDS spectra of the PP, PP@TiO₂, and As(III) adsorbed PP@TiO₂, are shown in Figure 1d–f, respectively. As seen in Figure 1d, the main peaks corresponding to C, O, and Si were observed for the PP sample. After impregnation with TiO₂ (PP@TiO₂), new peaks related to Ti were observed (Figure 1e), suggesting that the TiO₂ had been successfully impregnated onto biomass. As a result of arsenic adsorption, another peak belonging to arsenic was observed in the EDX spectra of As(III) adsorbed PP@TiO₂ (Figure 1f). This verified that PP@TiO₂ have successfully adsorbed arsenic from aqueous solution. The adsorption product was termed as As(III) adsorbed PP@TiO₂ and abbreviated as As//PP@TiO₂ hereafter.

Figure 2a shows the result of the XRD pattern of PP and PP@TiO₂. There were no sharp peaks of PP indicating the amorphous nature. In the case of PP@TiO₂, the diffraction peaks attributed to crystalline TiO₂ appear at $2\theta = 25.2^\circ, 38.1^\circ, 48^\circ, 55^\circ, 63^\circ, 70^\circ$, and 75° . These peaks correspond to the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 0 4), (2 2 0), and (2 1 5) planes, respectively. This confirms the successful impregnation of TiO₂ in the crystalline anatase form in biomass. The peaks show good agreements with JCPDS, card No. 21-1272 of anatase phase of TiO₂ [56–58]. The confirmation of the functional groups on adsorbents was done using FTIR spectra as shown in Figure 2b. It was examined in the ATR mode of FTIR. In the case of PP, absorption bands observed at around 3346, 2915, 1735, and 1621 cm^{−1} are attributed to –OH, –CH₂, –COO, and C=O stretching, respectively. The bands with the highest intensity located at 1023 cm^{−1} correspond to the C–O stretching of the hydroxyl functional group connected to the carbon atom. In the case of PP@TiO₂, the absorption peaks between 420 and 700 cm^{−1} ascribed to the Ti–O vibration representing the interaction of TiO₂ with biomass [54,56]. This provides clear evidence about the impregnation of TiO₂ and the formation of the Ti–O–C bond. The intensities

of bands of the aforementioned oxygen-containing functional groups of PP@TiO₂ were significantly decreased as compared to PP, indicating that loading of TiO₂ onto PP. After arsenic adsorption, at the FTIR spectra of As//PP@TiO₂, a new band observed at 825 cm⁻¹, corresponding to As–O stretching vibrations. This confirms As(III) adsorption onto PP@TiO₂. A similar phenomenon has been reported for arsenic adsorption onto nano scaled activated carbon modified by iron and manganese oxide [59].

Figure 1. (a) SEM image of PP; (b) SEM image of PP@TiO₂; (c) SEM image of As(III) adsorbed PP@TiO₂; (d) EDS spectra of PP; (e) EDS spectra of PP@TiO₂; (f) EDS spectra of As//PP@TiO₂.

Figure 2. (a) XRD spectra of PP and PP@TiO₂; (b) FTIR spectra of PP, PP@TiO₂, and As//PP@TiO₂.

2.2. Adsorption Isotherm

To investigate the quantitative As(III) adsorption capacity of PP@TiO₂, adsorption isotherm experiments were carried out using batch methods within a broad range of As(III) concentrations (V/m = 1000 mL/g, pH ~ 7). The initial and equilibrium concentrations of As(III) in solution are measured by inductively coupled plasma-mass (ICP-MS) spectroscopy. The obtained concentrations were used to calculate the % adsorption (A%, from Equation (1)) and the adsorption capacity of PP@TiO₂ (q_e, from Equation (2)).

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

$$q_e = \frac{(C_o - C_e) V}{m} \quad (2)$$

where, V, m, C_o, and C_e indicate the volume of As(III) solution (mL), amount of PP@TiO₂ taken (g), initial concentration (mg/L), and equilibrium concentration (mg/L) respectively. The distribution coefficient (K_D) is used to express the chemical binding capacity of an adsorbent and is stated as the ratio of the concentration of arsenic adsorbed in per gram of the adsorbent and its concentration per mL in the aqueous phase. It was expressed according to Equation (3) [60].

$$K_D = \left(\frac{V}{m} \right) \frac{(C_o - C_e)}{C_e} \quad (3)$$

The equilibrium data are presented in Figure 3a. Past studies have reported that adsorbents having a K_D value of 10³ mL/g are considered good adsorbent [61]. K_D values for the adsorption of As(III) obtained are in the order of ~10³ mL/g (see Figure 4b), which indicates that As(III) binds efficiently to the adsorbent.

Figure 3. (a) Adsorption isotherm of As(III) using PP@TiO₂ from water; (b) modeling of experimental data using Langmuir isotherm; (c) modeling of experimental data using Freundlich isotherm; (d) variation of R_L with initial As(III) concentration. (Conditions: V/m = 1000 mL/g, concentration of As(III) = 10–600 mg/L, pH = 7, T = 25 °C, contact time = 24 h).

Figure 4. Effect of pH for the adsorption of As(III) using PP@TiO₂ from water: (a) Adsorption % of As(III) by PP@TiO₂; (b) Distribution coefficient (K_D) of As(III) adsorption at different pH. (Conditions: $m = 25$ mg, $V = 25$ mL, $V:m = 1000$ mL/g, $T = 25$ °C, contact time = 24 h).

The equilibrium data were fitted using two binding models, Langmuir and Freundlich. The Langmuir model assumes the saturated monolayer adsorption on the homogenous and energetically identical adsorption sites, and no significant interaction between adsorbed species, which is expressed according to Equation (4) in the linear form [62] as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (4)$$

where, q_e (mg/g) is the amount of As(III) adsorbed at equilibrium concentration C_e (mg/L), q_m (mg/g) is the maximum adsorption capacity of adsorbent, and b (L/mg) is the Langmuir equilibrium constant related to adsorption energy. The q_m and b were determined from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e presented in Figure 3b.

Freundlich model considers a heterogeneous sorption surface and sorption sites with a different energy, which can be expressed by Equation (5) in its linear form [63] as:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

where K_F (mg/g) and n (L/mg) are Freundlich constants that indicate the adsorption capacity and the adsorption intensity, respectively. The two constants K_F and n were calculated from the slope ($1/n$) and intercept ($\log K_F$) of the Freundlich isotherm plot of $\log C_e$ versus $\log q_e$ presented in Figure 3c. The evaluated values of the isotherm parameters of both models are listed in Table 1. It is obvious from the result that the PP@TiO₂ is a suitable adsorbent for the adsorption of As(III) from water. For good adsorbent, the value of Freundlich constant (n) ranged between 1 and 10 (i.e., $1/n < 1$). It is evident from Table 1 that the value of ' n ' was found to be 2.72, indicating a strong adsorbent-adsorbate interaction. This tells us that the result obtained from Freundlich isotherm certainly cannot be neglected. Thus, both Langmuir and Freundlich isotherms showed a good fit to the experimental equilibrium data. The value of correlation coefficients (R^2) shows that the Langmuir model is better fitted than the Freundlich isotherm model. A similar observation was reported by Chandra et al. [64] for arsenic adsorption on magnetite reduced graphene oxide and Shehzad et al. [9] for As(III) adsorption on ZrO₂ nanosheets. These results indicated that the adsorption of As(III) onto PP@TiO₂ was not governed by a single mechanism.

Table 1. Langmuir and Freundlich isotherm parameters for the adsorption of As(III) onto PP@TiO₂.

Adsorbate	Adsorbent	Langmuir Model			Freundlich Model		
		q _m (mg/g)	b (L/mg)	R ²	K _F (mg/g)	n	R ²
As(III)	PP@TiO ₂	76.92	0.03	0.999	8.72	2.72	0.954

The observed maximum As(III) adsorption capacity, q_m, 76.92 mg/g compares well with previously reported materials for Arsenic adsorption, which are listed in Table 2. This comparison indicates that the adsorption capacity of PP@TiO₂ is higher than that of previously studied adsorbents [9,16–18,21,37,42,44,65–70]. Hence, the prepared PP@TiO₂ may be a promising material towards the removal of As(III) from water.

Table 2. Comparison of the maximum adsorption capacity (q_m) of different adsorbents for As(III).

Adsorbent	Optimum pH	q _m (mg/g)	Reference
Orange juice residue	10.0	68.16	[21]
Watermelon rind	8.2	3.40	[42]
Thiol functionalized sugarcane bagasse	7	28.57	[44]
Granular titanium dioxide	7	32.4	[37]
Fe ₃ O ₄ nanoparticles	7	46.06	[65]
Iron-modified activated carbon	7.6–8.0	38.8	[66]
Amorphous iron hydroxide	6–8	28.0	[67]
Fe ₃ O ₄ /sugarcane bagasse activated carbon composite	8	6.69	[16]
ZrO ₂ nanosheets	6	74.9	[9]
Iron modified bamboo charcoal	4–5	7.23	[68]
Fe(III) loaded pomegranate waste	9	50.0	[18]
Al-based MOF graphene-oxide nanocomposite	6.1	65.0	[17]
ZrO ₂ -sawdust	7	29.0	[69]
Copper-impregnated coconut husk carbon	6.5	20.35	[70]
TiO ₂ impregnated pomegranate peels (PP@TiO ₂)	7	76.92	This study

The feature of Langmuir isotherm was further justified by the analysis of the dimensionless separation factor, R_L, [71], which is given by Equation (6).

$$R_L = \frac{1}{1 + (bC_0)} \quad (6)$$

where b (L/mg) is Langmuir equilibrium constant and C₀ (mg/L) is the initial concentration of As(III). The value of R_L maybe 0, 1, or >1 indicating irreversible, linear, and unfavorable adsorption respectively. From the experimental data for all the concentrations tested, the evaluated R_L values were ranges from 0.06 to 0.76 (see Figure 3d). All of these values lie between 0 and 1 (0 < R_L < 1), which indicates more favorable adsorption of As(III) onto PP@TiO₂.

2.3. Effect of pH and As(III) Adsorption Mechanism

The % adsorption of As(III) and distribution coefficient, K_D onto PP@TiO₂ evaluated in the pH range of 2–12 are presented in Figure 4a,b, respectively, which show that the effective pH range for As(III) adsorption is from 6 to 9. A maximum K_D value of 3.21 × 10³ mL/g with the highest As(III) adsorption capacity of 81.4% is observed at pH 7. On increasing pH of the solution from 2 to 7, As(III) adsorption increased and then decreased beyond the pH 7. At lower pH values, As (III) exists only as neutral H₃AsO₃ species, and the surfaces of PP@TiO₂ are protonated. Thus, binding of As (III) on positively charged adsorbent is not favorable [20]. The adsorption of As(III) species took place via both electrostatic attraction and ligand exchange of the hydroxyl ions or water molecules contained in the coordination spheres of impregnated TiO₂ from the biomass surface. At higher than 10 pH values,

the predominant As(III) species H_2AsO_3^- , HAsO_3^{2-} and AsO_3^{3-} are repelled by the negatively charged adsorbent surface and therefore lower adsorption of As(III) has been obtained [21]. The decrease in As(III) adsorption can be attributed to the combined effect of electrostatic repulsion and the competition between the hydroxyl ions, and anionic arsenic species for adsorption sites. This is in agreement with the observation reported for As(III) adsorption from aqueous solution using iron oxide/nano-porous carbon magnetic composite [16].

Mechanism of As(III) adsorption using PP@TiO₂ can be described as follows. Impregnation with TiO₂ results in the generation of additional adsorption sites on the exterior surface of PP@TiO₂. It is inferred that during the impregnation of tetravalent Ti, neutralization of all the four positive charges of Ti by the functional groups (–OH, –COOH) present in biomass is difficult because of steric hindrance. Therefore, one or two positive charges of tetravalent Ti bind with a carboxylic acid or other functional groups in pomegranate peel biomass, and the rest are neutralized with hydroxyl ion. Thus, TiO₂ in aqueous solution undergoes a hydration reaction to give hydrated titanium oxide, Polymer $\equiv \text{Ti}(\text{OH})_n(\text{H}_2\text{O})_{6-n}$ (Equation (7)). At near neutral as well as weakly alkaline conditions i.e., at pH 6 to 9, As(III) exists as anionic species H_2AsO_3^- and HAsO_3^{2-} as well as neutral H_3AsO_3 molecule [20]. The adsorption of As(III) on PP@TiO₂ may be considered as a ligand exchange mechanism by the substitution of hydroxyl anions or neutral H₂O molecules. Thus, the undermentioned mechanism may be responsible for the sorption of anionic species (Equation (8)) and neutral species (Equation (9)) of As(III).

Besides, As(III) could be partially oxidized to less toxic and more easily adsorbed As(V) by the simple interaction with TiO₂ on the surface of the adsorbent, in batch experiments performed under room conditions [37]. The oxidized As(V) species, H_2AsO_4^- would be adsorbed according to Equation (10).

A similar mechanism has also been reported by Biswas et al., [20] for the removal of arsenic using Zr(IV) loaded orange waste gel. Joshi et al., [16] also reported a ligand exchange mechanism for As(III) onto Fe₃O₄/sugarcane bagasse activated carbon composite.

2.4. Adsorption Kinetics

To understand the dynamics of adsorption, the time variation in the amount of adsorption of As(III) on PP@TiO₂ was measured. Figure 5a shows the equilibrium concentration and adsorption percentage of As(III) as a function of contact time. Figure 5b exhibits the adsorption capacity (q_t) of As(III) with contact time on PP@TiO₂. The adsorption for As(III) reaches equilibrium within ~6 h. Therefore, 24 h was chosen as an optimum agitation period to achieve the complete adsorption of As(III) on PP@TiO₂ in the subsequent adsorption experiments. The kinetic data were fitted with pseudo-1st-order and pseudo-2nd-order models, which are expressed respectively [72] as Equations (11) and (12) below.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (11)$$

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

where q_e and q_t (mg/g) are the amount of As(III) ions adsorbed per unit mass of PP@TiO₂ at equilibrium and time t , respectively, and k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the rate constants of pseudo-1st-order and pseudo-2nd-order adsorption kinetics model. The pseudo-1st-order kinetic plot of $\log(q_e - q_t)$ versus t (Figure 5c) gives a linear relationship from which k_1 and q_e can be measured from the slope and intercept, respectively. Similarly, the pseudo-2nd-order kinetic plot t/q_t versus t (Figure 5d) gives a linear relationship from which k_2 and q_e can be measured from the intercept and slope, respectively. The kinetic parameters of As(III) adsorption evaluated based on both equations and R^2 are listed in Table 3. The pseudo-2nd-order kinetics is suitable for As(III) adsorption due to the higher value of R^2 (0.999), indicating the adsorption is chemisorption.

Figure 5. Adsorption kinetics curves for As(III) using PP@TiO₂: (a) equilibrium concentration and % adsorption of As(III) as a function of time; (b) adsorption capacity (q_t) with contact time; (c) pseudo-1st-order kinetics plot for As(III) adsorption; (d) pseudo-2nd-order kinetics plot for As(III) adsorption. (Conditions: $m = 25$ mg, $V = 25$ mL, $V/m = 1000$ mL/g, concentration of As(III) = 30.20 mg/L, pH = 7, $T = 25$ °C).

Table 3. Kinetic parameters for the adsorption of As(III) onto PP@TiO₂.

Order	Adsorbate	R^2	q_e (exp) (mg/g)	q_e (cal) (mg/g)	k_1 (min ⁻¹)	k_2 (mg/g/min)
Pseudo-2nd	As(III)	0.999	24.7	25.51	—	1.32×10^{-3}
Pseudo-1st	As(III)	0.932	24.7	15.45	9.85×10^{-3}	—

2.5. X-ray Photoelectron Spectroscopy (XPS) Studies

The surface composition and chemical states of the PP@TiO₂ after As(III) adsorption experiments were further analyzed by the XPS. The wide scan spectrum indicated signals from Ti, O, C, and As in the sorption product (Figure 6a). The high-resolution XPS scan of Ti 2p (Figure 6b) showed two broad peaks centered at ~458.6 and 467.3 eV representing the Ti 2p_{3/2} and Ti 2p_{1/2} peaks of Ti⁴⁺, respectively [56]. Additional peaks at about 457.25 eV and 463.27 are attributed to the Ti 2p_{3/2} and Ti 2p_{1/2} peaks of Ti³⁺, respectively [73]. The Ti 2p spectrum mainly appears in Ti⁴⁺ state with a small amount of Ti³⁺.

The occurrence of Ti^{3+} is due to oxygen deficiency in the lattice of TiO_2 [73]. This indicated a reduction of Ti^{4+} to Ti^{3+} during the partial oxidation of adsorbed As(III). The high-resolution XPS scan of As 3d (Figure 6c) was composed of two peaks indicating the presence of both As^{3+} (B.E. = 44.32 eV) and As^{5+} (B.E. = 46.24 eV) with a qualitative ratio of 75.7% and 24.3%, respectively. Hence, the partial oxidation of As(III) by impregnated TiO_2 was verified by XPS using As 3d spectrum [74]. The high-resolution XPS scan of O 1s (Figure 6d) was composed of peaks at ~528.4, 529.9, and 531.8 eV are associated with Ti–O, O–As, and O–H bonds, respectively.

Figure 6. XPS spectra of PP@TiO₂ after As(III) adsorption: (a) Wide scan; (b) Ti 2p; (c) As 3d; (d) O 1s.

Thus, XPS results revealed that As(III) is adsorbed onto PP@TiO₂ and is partially oxidized to As(V). Similar behavior was reported by Tamayo et al. [19] for As(III) removal from aqueous solution on calcium titanate nanoparticles. The partial oxidation of As(III) to As(V) could be due to the presence of physio-sorbed oxygen and surface hydroxyl groups. All results revealed that PP@TiO₂, on one hand, can remediate As(III) from water, and on the other hand, it can oxidize some of the As(III) to As(V) at the surface of the adsorbent simultaneously. Previous studies have reported that the degree of photocatalytic oxidation of As(III) to As(V) under the influence of TiO₂ photocatalyst highly dependent on various operation factors such as pH, dissolved oxygen, initial As(III) concentration, a wavelength of light, the intensity of light, TiO₂ loading, calcination temperature, properties of TiO₂ (bandgap, particle size), presence of coexisting ions and batch reactor configuration [32,75]. Bang and Patel [37] reported that around 10% of As(III) is oxidized to less toxic and more easily adsorbed As(V) by the simple interaction with TiO₂, in batch experiments performed under room conditions. Yao et al. [32] reported that 0.80 mg/L of As(III) could be completely oxidized to As(V) within 30 min in the presence of 3.0 g/L TiO₂/ACF (composite of TiO₂ and activated carbon fiber) in the irradiation of UV-light. They observed that the presence of silicate and phosphate ions significantly decreased the oxidation of

As(III). Past studies have reported the complete oxidation of As(III) to As(V) by TiO₂ in the presence of UV light and oxygen [30,34]. The As(III) adsorption and photo-oxidation capability of biomaterial/TiO₂ composite increases as n-TiO₂ loading [53]. Nevertheless, additional research is required to investigate detailed As(III) oxidation characteristics of PP@TiO₂.

2.6. Effect of Common Coexisting Anions

The effect of common coexisting anions on As(III) adsorption from aqueous solution was examined considering various concentrations of chloride (Cl[−]), sulphate (SO₄^{2−}), and phosphate (PO₄^{3−}). As shown in Figure 7, compared to the blank (no coexisting ions), an increase in the concentration of coexisting ions leads to a decrease in As(III) adsorption efficiency for all the tested ions. Minimal interference was observed in the presence of Cl[−], while the stronger interference was observed for PO₄^{3−} that reaches % adsorption loss up to 27.9% at its highest concentration (100 mg/L). Hence, phosphate is the strongest competitor with arsenic ions to binding sites on PP@TiO₂. This can be attributed to the similar oxyanion structure of both phosphate and arsenic anions [76].

Figure 7. Effect of common coexisting anions on adsorption of As(III) using PP@TiO₂. (Conditions: Coexisting ions concentration = 10, 50, 100 mg/L; initial As(III) concentration = 25 mg/L; pH = 7; V:m = 1000 mL/g, T = 25 °C, contact time = 24 h).

2.7. Desorption Study and Reusability of PP@TiO₂

Desorption of As(III) from As//PP@TiO₂ is important to assess the recovery of toxic arsenic and regeneration of spent adsorbents for repeated use. Desorption tests were carried out by batch method using the adsorbent loaded with As(III) immediately after the adsorption processes. As shown in Figure 4, As(III) is efficiently adsorbed on PP@TiO₂ at pH range 6–9 but it is poorly adsorbed at higher pH (>9), indicating that desorption of adsorbed As(III) can be easily achieved by employing the weakly alkaline solution. Consequently, the desorption test was carried out with different concentrations of NaOH ranging from 0.01–0.5 M as presented in Figure 8a. The % desorption (% D) of As(III) was calculated using Equation (13) as follows [77].

$$\% D = \frac{D_{\text{amount}}}{A_{\text{amount}}} \times 100 \quad (13)$$

where, A_{amount} and D_{amount} are the adsorbed and desorbed amounts (mg) of As(III) ions, respectively. The desorption of arsenic increases from 29.1% to 97.8% by increasing the concentration of NaOH

from 0.01 to 0.1 M and remains constant with a further increase in concentration. Hence, a 0.1 M NaOH solution was found to be a suitable desorbing agent for the regeneration of spent adsorbent. Hydroxyl ions released from the NaOH solution might have replaced the adsorbed arsenic anions onto the PP@TiO₂ surface. The desorption of arsenic species is believed to take place by the ligand substitution mechanism by the replacement of adsorbed arsenic species by hydroxyl ions in alkali solution as shown below (Equation (14)).

Figure 8. (a) Desorption of arsenic from arsenic loaded PP@TiO₂. (Conditions: weight of loaded PP@TiO₂ = 25 mg, volume of eluent = 25 mL, V/m = 1000 mL/g, adsorbed amount of arsenic = 20.34 mg/L, T = 25 °C, contact time = 24 h); (b) variation of the adsorption capacity of the PP@TiO₂ in subsequent adsorption-desorption cycles of As(III).

To evaluate the reusability of the PP@TiO₂, it was subjected to four series of adsorption/desorption cycles. Figure 8b shows that the initial adsorption capacity of As(III) was decreased by 14.5% after four cycles. This result indicated that the PP@TiO₂ exhibited excellent stability and reusability. In alkaline solution, the surface of the adsorbent becomes negatively charged and As(III) anions are displaced by OH[−], leaving the sorption sites before the succeeding adsorption cycle without affecting the chemical stability of the adsorbent. The high desorption efficiency of arsenic from the PP@TiO₂ created the low-cost removal technique since both adsorbent and arsenic were regenerated and recycled efficaciously.

3. Materials and Methods

3.1. Materials

Analytical grade chemicals were used without additional purification. The waste biomass of pomegranate peels employed in this study was collected from a local juice vendor, Kathmandu, Nepal. All the solutions in the study were prepared using deionized water. Sodium arsenite (NaAsO₂) (Sigma–Aldrich, New Delhi, India), titanium(IV) n-butoxide (Samchun pure chemical, Seoul, Korea) were used. A standard stock solution of As(III) (1000 mg/L) was prepared by dissolving an exact amount of NaAsO₂ in deionized water and stored in the refrigerator for further use.

3.2. Synthesis of TiO₂ Impregnated Pomegranate Peels (PP@TiO₂)

The pomegranate peel waste was kindly donated by a local juice vendor, Kathmandu, Nepal. Pomegranate peels were first washed thoroughly with distilled water. It was then oven-dried at

70–80 °C for 48 h. The dried mass was grounded and sieved through (150 µm) mesh copper sieve. To avoid the dissolution of the adsorbent in aqueous solutions, polyphenol and polysaccharide hydroxyl groups in the biomass were cross-linked through condensation reaction using concentrated sulfuric acid as a dehydrating agent. The cross-linked pomegranate peels were prepared as described in Paudyal et al., [78]. 15 g of this biomass powder was mixed with 30 mL of concentrated H₂SO₄ (96%) in a round bottom flask and the mixture was agitated for 24 h at 100 °C followed by cooling at room temperature. The black product was then neutralized with sodium bicarbonate and reconditioned by stirring again in 1 M HCl solution. It was washed several times with distilled water till neutrality, after which it was dried overnight in a convection oven at 70 °C. The pomegranate peels powder obtained in this way is abbreviated as PP.

The PP@TiO₂ was prepared using a previously reported modified sol-gel method [73,79–81]. About 10 mL of titanium(IV) n-butoxide was mixed with 15 mL of ethanol. After stirring for 30 min at room temperature, 2 g of powdered PP was added to it. Then, 15 mL of a solution of 1:1:1 ethanol, deionized water, and acetic acid were added dropwise from the burette to the magnetically stirred mixture. The whole content was further stirred for 4h until sol was obtained. The sol was dried overnight at 80 °C after aging at 40 °C for 2 h. Finally, the dried gel was ground into a powder and calcined at 400 °C in a muffle furnace for 2 h. The resulting PP@TiO₂ was stored in a plastic container before being used in the characterization and adsorption experiment.

3.3. Characterizations

To investigate the morphology and elemental composition of adsorbents, SEM images and EDS were carried out on a JEOL JSM–6700F instrument (Jeol Ltd., Tokyo, Japan) equipped with X-ray Energy Dispersive Spectrometer. The crystallinity of PP@TiO₂ samples was investigated by XRD, Rigaku Ultima IV X-ray diffractometer (Rigaku Co., Tokyo, Japan) with Cu Kα ($\lambda = 1.54056 \text{ \AA}$) radiation. The surface functional groups of samples were analyzed using FTIR spectroscopy on IR AFFINITY-1 Shimadzu (Shimadzu, Kyoto, Japan) spectrometer in the wavenumber range of 400–4000 cm^{−1}.

3.4. Batch Adsorption Studies

The adsorption studies for As(III) were carried out to examine the adsorption behavior on the PP@TiO₂ using the batch method (V: m~1000 mL/g). 25 mg (dry weight) of PP@TiO₂ was taken in different 50 mL conical flasks containing 25 mL of As (III) solution in the concentration range 10–600 mg/L and shaken for 24 h at 25 °C to attain equilibrium. The pH of the As(III) solution was maintained with 0.1M HCl and 0.1 M NaOH solutions. After adsorption, the PP@TiO₂ was separated from the mixture by filtration and dried at 70 °C. The initial and equilibrium concentration of arsenic was analyzed. From the equilibrium concentration, the sorption isotherms and maximum adsorption capacity were evaluated. Two isotherms model, Langmuir, and Freundlich were used to describe the As(III) sorption behavior.

Effect of pH: The influence of pH of the solution on the sorption of arsenic was investigated over the pH range 2–13. 25 mg of PP@TiO₂ was shaken for 24 h in 25 mL solution of 20–25 mg/L As(III) with varying pH solutions, prepared by using 0.1M HCl and 0.1M NaOH solutions. The resulting solution was analyzed for the equilibrium concentration.

Adsorption Kinetics: Kinetic studies of As(III) adsorption on to PP@TiO₂ were carried out until it reached equilibrium. For each experiment, 25 mg of the PP@TiO₂ was taken in a 50 mL conical flask containing 25 mL of ~30 mg/L As(III) aqueous solution (V/m = 1000 mL/g) at pH 7, and the content was shaken well at room temperature. Adsorption experiments of various contact times were performed. After a predetermined time interval, the sample of each flask was immediately filtered and the equilibrium concentration of As(III) was analyzed.

Effects of Common Co-existing Ions: Natural water contains several coexisting ions, which may compete with As(III) for available active sorption sites and affect the As(III) adsorption efficiency of PP@TiO₂. The effect of common coexisting anions in an aqueous system such as Cl[−], SO₄^{2−}, and PO₄^{3−} on the

adsorption of As(III) was examined by adding various concentrations (10, 50, and 100 mg/L) of each coexisting ions into 25 mg/L As(III) solution as a binary mixture. To prepare various concentrations of coexisting ion solutions, different potassium salts (KCl, K₂SO₄, and KH₂PO₄, 99% pure, Merk, Kenilworth, NJ, USA) were used. Additionally, the blank sample was made similarly without adding coexisting anion. The pH of all the solutions was maintained to 7.0 by using 0.1M HNO₃ and 0.1M NaOH. A defined amount (1 g/L) of PP@TiO₂ was added and the mixtures were shaken for 24 h at 25 °C to attain equilibrium. After filtration, the remaining concentration of As(III) was analyzed.

3.5. X-ray Photoelectron Spectroscopy (XPS) Studies

To elucidate chemical composition and arsenic speciation, the XPS investigation of sorption product was carried out on Kratos Axis Ultra DLD spectrometer (Kratos Analyticals, Manchester, UK) with a monochromatic Al K α X-ray source (150 W). Samples were mounted using double-sided adhesive tape, and binding energies were referenced to the C 1s binding energy of adventitious carbon taken to be 286.4 eV. For the survey of elements, the wide scans were taken at pass energy of 80 eV, and scans of photoelectron peaks were taken at pass energy of 40 eV.

3.6. Desorption Study and Reusability of PP@TiO₂

For the desorption study, As(III) adsorbed PP@TiO₂ was prepared by shaking 250 mg of PP@TiO₂ with 250 mL of As(III) solution (25 mg/L) at pH 7 for 24 h at room temperature. After filtration, the filtrate was examined for residual As(III) concentration. From initial and residual concentration, the adsorbed amount of As(III) was evaluated. The filter cake was dried. The dried As(III) adsorbed PP@TiO₂ was used for the elution test. The adsorbed arsenic was effectively eluted by the alkali solution. To identify the optimum concentration of alkali, 25 mg of exhausted PP@TiO₂ was shaken with 25 mL of various concentrations of NaOH solution ranging from 0.01 to 0.5 M batch-wise, similar to adsorption studies. The sample of each flask was filtered and the filtrate was analyzed for the desorbed amount of arsenic. The % desorption was calculated. Four cycles of adsorption/desorption of As(III) were carried out to investigate the reusability of PP@TiO₂. The PP@TiO₂ samples after the adsorption process were stirred with 0.1M NaOH solution followed by filtration, washing with deionized water, and drying. The regenerated PP@TiO₂ was again used for the adsorption experiments to evaluate reusability up to four times.

3.7. Analysis of Arsenic Concentration

For all the above experiments, the initial and equilibrium concentration of arsenic in the solution was analyzed by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Agilent Technologies, 7900 ICP-MS, Santa Clara, CA, USA) with argon plasma, and internal standards of germanium and scandium. For the calibration of the instrument, a repeating As(III) standard and blank were analyzed every 10 samples. Before analysis, all samples were acidified with 1% HNO₃ and analyzed within 48 h.

4. Conclusions

In summary, we herein synthesized PP@TiO₂ using a modified sol-gel method, which was then applied as an efficient adsorbent for removal of As(III) from water. Based on the results of characterizations, it was reasonable to conclude the effective loading of TiO₂ into biomass and successful adsorption of As(III) onto PP@TiO₂. The maximum adsorption of As(III) on PP@TiO₂ was observed at neutral pH with a high distribution coefficient of 4.0×10^3 mL/g. The equilibrium data were better followed by the Langmuir-model, which indicated that the monolayer adsorption of As(III) occurred on a homogenous surface of the PP@TiO₂. The maximum adsorption capacity for As(III) was evaluated as 76.92 mg/g, which was found to be higher than many other agro-waste based bio-adsorbents and bare TiO₂ reported in the literature. Kinetics data showed that the adsorption followed the pseudo-second-order model, suggesting the process might be chemisorptions with higher initial adsorption rates. The XPS analysis of PP@TiO₂ after the As(III) adsorption process revealed that

the adsorbed species was present as As(III) and partially oxidized to As(V). Moreover, the PP@TiO₂ can work effectively in the presence of various coexisting anions, and the exhausted PP@TiO₂ can be easily separated for regeneration and reuse. PP@TiO₂ is a safe substance for human health and a feasible low-cost material. Thus, PP@TiO₂ investigated in this study can be considered an efficient, cost-effective, environmentally friendly, and reusable adsorbent for removing As(III) from water.

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