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Apple Peels—A Versatile Biomass for Water Purification?

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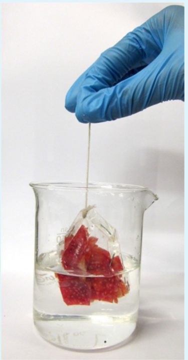
ABSTRACT: The presence of anions such as chromate, arsenate, and arsenite in drinking water is a major health concern in many parts of the world due to their high toxicity. Removal of such anions from water using low cost biomass is an efficient and affordable treatment process. Owing to the easy availability and biodegradability, we chose to use apple peel as a substrate for our investigations. Zirconium cations were immobilized onto the apple peel surface and used for the extraction of anions. Zirconium loaded apple peels were used to extract anions such as phosphate, arsenate, arsenite, and chromate ions from aqueous solutions. The presence of Zr cations on the apple peel surface was characterized using XPS. The modified adsorbent was characterized using SEM, EDS, and FT-IR. Zr treated apple peels showed efficient adsorption toward AsO_2^- (15.64 mg/g), AsO_4^{3-} (15.68 mg/g), $Cr_2O_7^{2-}$ (25.28 mg/g), and PO_4^{3-} (20.35 mg/g) anions. The adsorption and desorption studies revealed the adsorption mechanism involves electrostatic interactions. Anion removal efficiency was estimated by batch adsorption studies. Adsorption kinetic parameters for all anions at different concentrations were described using pseudo-first-order and pseudo-second-order rate equations. Langumir and Freundlich isotherms were used to validate our adsorption data. Arsenate and chromate anions were strongly adsorbed at the pH range from 2 to 6, while arsenite was extracted efficiently between pH 9 and 10. Overall, the Zr immobilized apple peel is an efficient adsorbent for common anionic pollutants.



KEYWORDS: *anions, apple peel, adsorption, isotherms, kinetics*

1. INTRODUCTION

Ground water contaminated with anions such as chromate ($Cr_2O_7^{2-}$), arsenite (AsO_2^-), arsenate (AsO_4^{3-}), and other anions has become one of the most serious problems throughout the world.[1] These oxoanions are known to be highly toxic even at low concentrations and can accumulate in the human body, causing various diseases and disorders.[2] These anions are considered as toxic contaminants found in water and can exist as various forms in the environment. Arsenic is present as arsenite (AsO_3^{3-}), and arsenate (AsO_4^{3-}) salts are common in natural waters. In chromate anion, chromium can exist in oxidation states from +2 to +6, but only Cr(III) and Cr(VI) are of environmental significance.[3] Long-term consumption of drinking water containing arsenic and chromium led to many health problems including cardiovascular effects, bladder, skin cancer, and anemia among populations in different parts of the world.[4−8] High levels of phosphate in wastewater disturb the nutrient equilibrium, leading to enhanced growth of aquatic plants and subsequent eutrophication of lakes and rivers.[9−11] Therefore, it is important to develop effective methods to remove such toxic anions from water.

Common water treatment technologies include filtration, precipitation, oxidation, coagulation, and anion exchange.[12−17] These methods are efficient in removing pollutants, including anions from aqueous media, but produce large amounts of toxic wastes that require further decontamination processes before disposal. Adsorption of anions onto an active surface has been considered as an efficient alternative method for purifying contaminated water.[18,19] Different adsorbents including activated alumina,[20] sand,[21] iron and manganese oxide or hydroxide,[22−24] hydroxyapatite,[25,26] activated carbon,[18,27] and biomaterials[19,28−31] were considered for the removal of anions. These adsorbents have different adsorption capacities that depend on the sorbent mass, pH, contact time, and initial concentration of the adsorbate in the solution. Adsorption of anions using biomass has emerged as a viable option for developing economic and eco-friendly wastewater treatment processes. Natural materials have been tested for removal of pollutants from water. A number of studies have shown the use of bioadsorbents including biochar,[32] fungal biomass,[33] chicken feathers,[34] methylated yeast biomass,[35] and alginate[36] to remove anions from aqueous solution. Many biopeels such as banana peel, orange peel, papaya peel, potato peel, water melon shell, and mango peel, to name a few, were exploited for the extraction of different pollutants.[29,30] In most cases, pollutants such as dyes, pesticides, and cations were extracted from water. Extraction of anions is much tougher than extraction of the other pollutants. Only a few reports exist on the use of fruit peels for anion extraction from water. A cationic adsorbent is needed to extract anions, and functionalization via chemical treatment methods is used to transform biopeels as efficient adsorbents for anion removal. Some of the surface modifcations involve immobilization of chitosan, PEI coating, and Fe or Zr cation loading. However, these modified biopeels were used for the extraction of a single anion. We used Zr immobilized apple peel to extract different anions efficiently. Metal cations such as La(III), Ce(IV), Fe(III), and Zr (IV) loaded orange waste were used for the extraction of arsenic and phosphate anions. Banana

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peel was reported for the extraction of chromate anion.[29] Lemon peel was used for the removal of anionic dyes.[30]

Advantages of biomembranes include low cost, nontoxic, easy processing, and presence of abundant functional groups. However, these biomembranes with surface functional groups such as −COOH and −OH can remove cationic pollutants more effectively than anion.[37] Therefore, adsorption based on ligand substitution with metal loaded adsorbents is gaining more attention. It is shown that loaded metal cations with high positive charges can bind oxoanionic species such as arsenate, arsenite,[9,38] and phosphate ions.[10,11] Removal of arsenic and chromium anions by using zirconium salt treated adsorbents was reported,[39] because zirconium in its hydrated form can generate tetranuclear ions as well as octanuclear species which have hydroxyl ions and water molecules to take part in ligand exchange with phosphate and arsenic species. Moreover, hydrated zirconium cations are resistant to attack by alkali acids, oxidants, and reductants.[40] Apple peels are available worldwide as biowaste from food processing industries and offer abundant functional groups which can be exploited for water treatment. Apples contain a large concentration of flavonoids of the procyanidins, catechin, epicatechin, chlorogenic acid, phloridzin, and the quercetin conjugates.[41,42] These functional groups from these compounds are expected to bind Zr(IV) strongly on the membrane surface. Here we discuss the development of an efficient adsorbent using a readily easily available apple peel immobilized with Zr(IV) ions on the surface for the extraction of multiple anions from aqueous media.

2. MATERIALS AND METHODS

Apples were bought from the local supermarket, and the outer layer was carefully peeled off and cut into small pieces of around 0.04 cm^2 in size. Raw peels were saponified with NaOH to cleave ester bonds and generate more hydoxyl groups. Deionized water washings were given to remove excess base. Washed peels were then sonicated in 2-proponol to extract leachable organics. The resulting adsorbent was washed with water and dried. Stock solutions of arsenite (AsO_2^-), arsenate (AsO_4^{3-}), chromate ($Cr_2O_7^{2-}$), and phosphate (PO_4^{3-}) anions were prepared by dissolving stoichiometric amounts of $NaAsO_2$, $Na_2HAsO_4{\cdot}7H_2O$, $K_2Cr_2O_7$, and $Na_3PO_4{\cdot}12H_2O$ in deionized water, respectively. Aqueous solutions of HCl (0.1 mol/L) and NaOH (0.1 mol/L) were used for pH adjustments. All chemicals and reagents used were AR grade and purchased from Sigma Aldrich.

2.1. Immobilization of Apple Peel. Zr(IV) (0.1 M) solution was prepared by dissolving $ZrO_2Cl{\cdot}8H_2O$ (3.22 g) in deionized water (100 mL). Dried apple peel (5 g) was added to Zr solution (100 mL, 0.1 M), and it was left for 6 h at room temperature at neutral pH. The Zr-loaded apple peel was then washed with copious amounts of water to remove excess ions from the surface. The peel was dried and used for characterizations and adsorption studies. This study was focused on the water treatment using Zr immobilized apple peels.

2.2. Characterization of Peels. Surface structures of the peel were captured using field emission scanning electron microscopy (JEOL JSM-6701F). Dried apple peels were coated with platinum metal before SEM analysis to make the surface conductive. Energy dispersive X-ray spectroscopy (EDS) was done in conjunction with SEM to investigate the chemical composition of the apple peel. The IR spectra were recorded in the range of 4000−400 cm^{-1} using a Bruker ALPHA FT-IR spectrophotometer with a resolution of 4.0 cm^{-1}. Specimens were first mixed with KBr powder and then grounded in an agate mortar. The mixture was pressed at 10 tons for 5 min to form a 100 mg disk using a KBr press model MP-15. Twenty scans were used for each spectrum. The concentrations of pollutants of experimental and control samples were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES), which was carried out using the Dual-view Optima 5300 DV ICP-OES system; for arsenic(III, V), and chromium(VI), the ion-exchange chromatography was employed, using the 818 IC Pump, 820 Separation Center, 830 Interface, 833 Liquid handling Unit, and 732 Detector and 813 Compact auto sampler for phosphate. Surface elements of the peels were identified using X-ray photoelectron spectroscopy (XPS) with a spatial resolution of 30 μm (Kratos XPS system, Axis His, 165 Ultra, Shimadzu, Japan). The C 1s signal of an adventitious carbon was used as reference to compensate for charging effect at a binding energy (BE) of 284.8 eV. The XPS results were collected in binding energy form, and data were analyzed using a nonlinear least-squares curve fitting program (XPSPEAK41 Software). The peak's full-width-at-half-maximum (fwhm) was fixed during the fitting.

2.3. Effect of Initial Adsorbate Concentration and Time. Apple peel (0.1 g) treated with Zr salt was added to solutions (10 mL) of different concentrations of pollutants. All adsorption experiments were done at 30 °C using an orbital shaker at 200 rpm. Singapore is a tropical country with a day time temperature of 30 °C, and we have carried out extractions at this temperature to assess the performance of adsorbents. In our previous studies,[37] an increase in temperature led to decrease in adsorption efficiency. The residual concentration of pollutants were analyzed after predetermined intervals of time until the system reached equilibrium. The pollutant adsorbed at equilibrium q_e (mg/g) was calculated by using the following equation.[31]

$$q_e = (C_0 - C_e)V/M \tag{1}$$

where C_0 and C_e (mg/L) are concentration of pollutant at initial stage and equilibrium conditions, V (L) is volume of the pollutant solution, and M (g) is mass of the adsorbent used. The initial concentrations of anionic solution used were 5, 10, 20, 40, 70, 100, and 200 mg/L, and the experiments were carried out for 24 h.

2.4. Kinetic and Isotherm Studies. Samples consisting of a portion (0.1 g) of the adsorbent material (apple peel) and various initial pollutant concentrations 5−200 mg/L were poured into the conical flask and agitated using an orbital shaker at 200 rpm at 30 °C. The time required to reach equilibrium was maintained as determined in equilibrium studies. The equilibrium adsorptions of anions were studied using Langmuir[33] and Freundlich[36] isotherm models. The rate of adsorption of different anionic pollutants on apple peels was measured by studying pseudo-first-order and pseudo-second-order kinetics of adsorption.

2.5. Effect of Solution pH. The solution pH effect on pollutant removal was studied by varying the pH from 2 to 12 using 0.01 N HCl or 0.01 N NaOH. The initial concentration used was 100 mg/L for all anions. Other parameters such as adsorbent dosage, agitation speed, and solution temperature remained constant. The percentage removal of pollutant was calculated as[31]

$$\text{removal } \% = \left(\frac{C_i - C_f}{C_i}\right)100 \tag{2}$$

where C_i and C_f (mg/L) are initial and final concentration of pollutants in the water.

2.6. Desorption Studies. Samples were prepared by adding pollutant adsorbed apple peel (0.1g) to solution (10 mL) of double distilled water. The solutions were equilibrated for different time periods and stirred constantly. Desorption studies were conducted at different pH values, and samples were analyzed at different time intervals. The concentrations of anionic pollutants were measured with ICP-OES and ion chromatography. Each experiment was repeated under identical conditions to check reproducibility.

3. RESULTS AND DISCUSSION

The chemical constituents of apple peels were well studied.[41] Apples mainly contain flavonoids of the procyanidins, catechin, epicatechin, chlorogenic acid, phloridzin, and the quercetin conjugates. The FT-IR spectra of apple peel in the range of 4000−400 cm^{-1} is shown in Figure 1. The broad band in the range of 3760−3204 cm^{-1} corresponds to the O−H bond

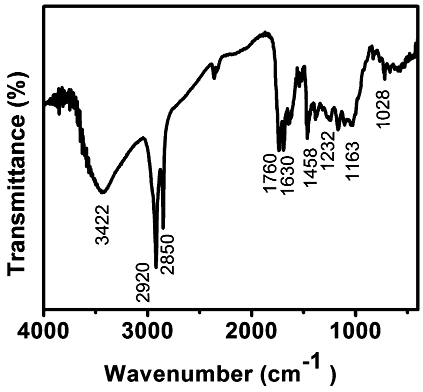

Figure 1. FT-IR spectrum of raw apple peel after washing with aqueous NaOH solution.

stretch of alcohols (usually between 3700 and 3200 cm^{-1}) and O−H bond vibration of carboxylic acids (3400 and 2400 cm^{-1}). The sharp peak at 2918 cm^{-1} and 1732 cm^{-1} corresponds to C—H and >C═O stretch, respectively. The absorptions in the ranges of 1600−1585 cm^{-1} and 1500−1400 cm^{-1} are accountable to stretching of C═C bond in the aromatic rings. The peaks due to the angular deformation in the plane of the C—H bonds of the aromatic rings (1300−1000 cm^{-1}), axial bending of C—O bond in phenols (1260−1000 cm^{-1}), and axial bending of C—O bond in —COOH (1320−1210 cm^{-1}) were visible in the spectrum. IR analysis of functional groups present in apple peel matches with reported literature values.[41] IR spectra of adsorbent were recorded before and after adsorption of different anions, and significant differences were not observed.

The SEM images of apple peel before and after chemical treatment are shown in Figure 2. Apple peel has a fibrous structure with a fiber diameter in the range of 9−25 μm with Zr nanoparticles bonded on the surface. EDS analysis (Figure 2) indicated carbon, oxygen, and sulfur atoms on the untreated peel surface and significant amounts of Zr on the treated surface. Figure 3a shows the XPS profile of Zr treated apple

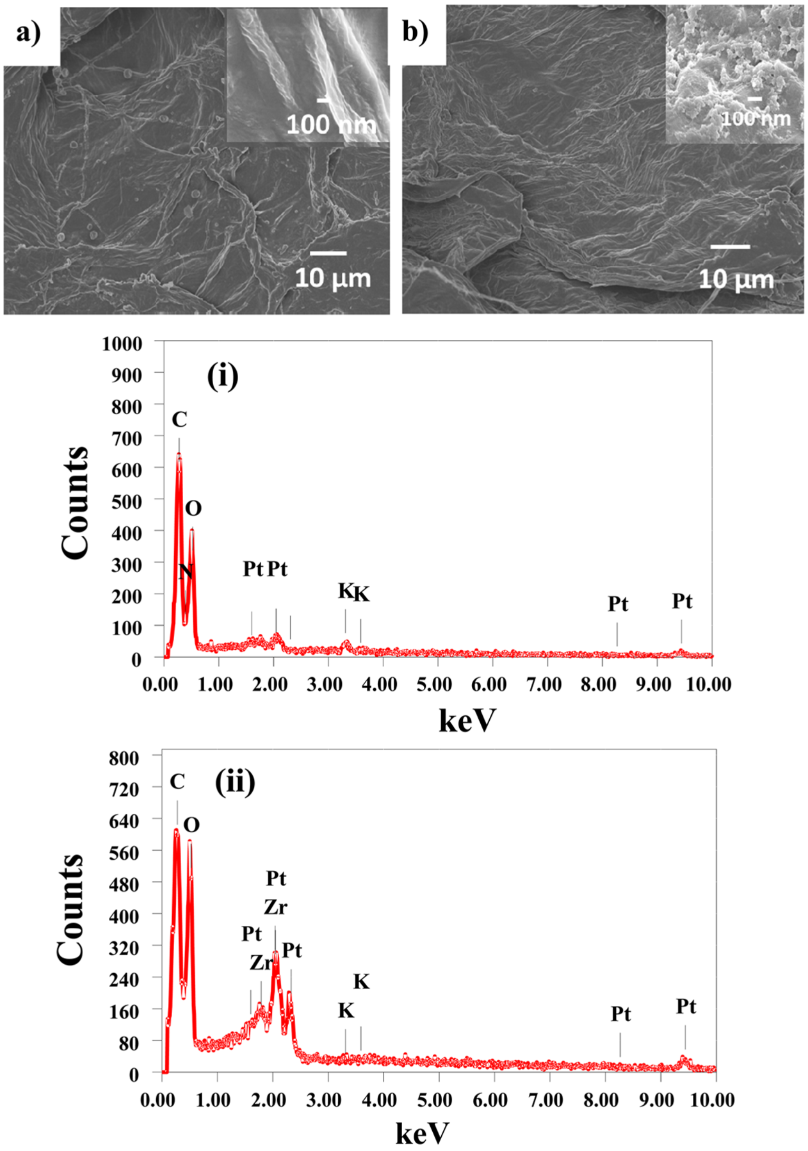

Figure 2. FESEM micrographs (a, b) and EDS (i, ii) analysis of apple peel surface before (a, i) and after (b, ii) Zr treatment. Insets in (a) and (b) show the magnified surface image.

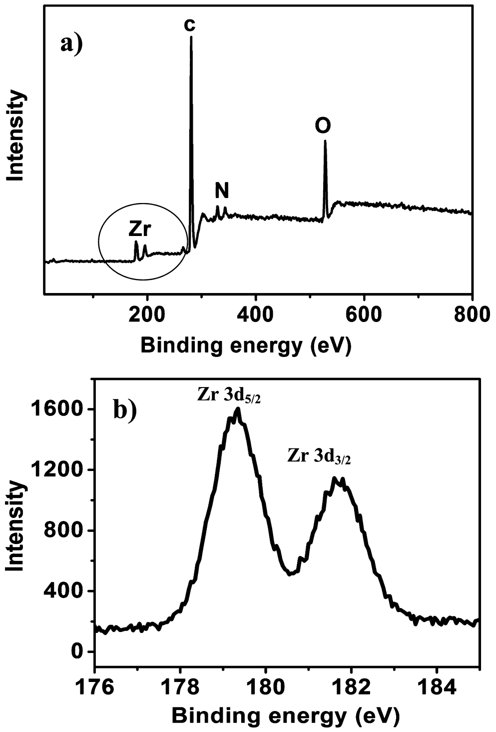

Figure 3. XPS profile (a) and expanded region for Zr peaks (b) of treated apple peel surface.

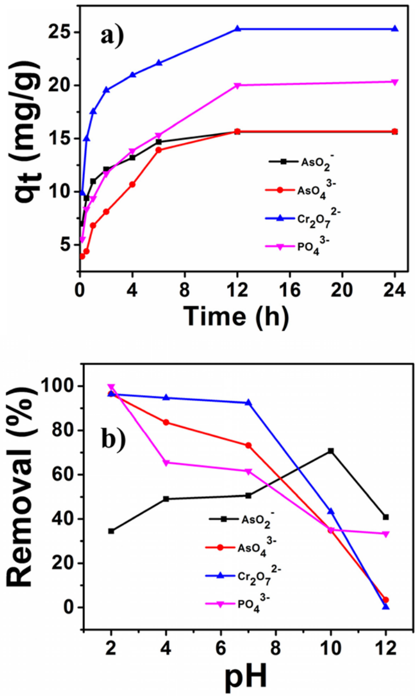

Figure 4. Variation of adsorption capacity of Zr treated apple peel toward different anions with change in time (a) and pH (b).

peel. The spectrum indicates the presence of carbon (281 eV, 1s), nitrogen (396 eV, 1s), oxygen (528 eV, 1s), and Zr (179 eV, 3d) on the surface of the apple peel. The peaks corresponding to the binding energies at 179 and 182 eV in Figure 3b clearly indicates that Zr is bonded to the apple peel surface and exists in (+) 4 oxidation state. This high positive charge of the Zr immobilized surface is responsible for the binding of anions.[43]

3.1. Effects of Initial Pollutant Concentration and Contact Time. The adsorption rate for different pollutants at 303 K is shown in Figure 4a. The amount of pollutant adsorbed (mg/g) increased with increase in time and reached equilibrium. The adsorption of chromate ($Cr_2O_7^{2-}$) is higher than arsenate (AsO_4^{3-}) and arsenite (AsO_2^{-}) which may be due to weak interactions of arsenate anions with the adsorbent.[29−31] The adsorption experiments were carried out for 24 h to evaluate equilibrium adsorption capacity (q_e mg/g) of each anionic pollutant. All anions reach equilibrium within 6 h which indicates faster adsorption. Chromate ions showed highest q_e (25 mg/g) followed by phosphate (18 mg/g) and arsenic (14 mg/g) ions. The results indicate that the Zr treated apple peel binds anionic pollutants efficiently, owing to the high positive charge of Zr cations on the surface.[43]

3.2. Effect of pH. The effect of pH on the adsorption of anions onto the Zr loaded apple peel is shown in Figure 4b, which shows that the adsorption of $Cr_2O_7^{2-}$, AsO_4^{3-}, and PO_4^{3-} reaches maximum at acidic pH but AsO_2^{-} shows higher adsorption at pH 10. On the basis of the data, pH 10 for AsO_2^{-} and pH 2 for other anions were selected for further batch-mode adsorption experiments. Release of Zr cations from the peel to the aqueous medium during adsorption studies was tested by analyzing Zr content in the adsorbate solution. Elemental analysis showed no detectable concentration of Zr in the solution. Arsenic and chromium can exist as different anionic species depending on pH of the solution The dominant species in the acidic pH range are $H_2AsO_4^{-}$, $HCrO_4^{-}$, $H_2PO_4^{-}$, and $HAsO_4^{2-}$ ions which can be adsorbed on the gel by substituting hydroxyl ions from the coordination sphere of the loaded Zr(IV).[43] Maximum adsorption of AsO_2^{-} was observed at a weakly alkaline environment from pH 9 to 10, and pH 10 was selected for further batch-mode adsorption experiments. This implies that monoanionic ($H_2AsO_3^{-}$) species are adsorbed by substituting hydroxyl ions or water molecules.[43] At high pH, adsorbates exist as oxoanions and no precipitation was observed. The decrease in arsenic adsorption at higher pH can be attributed to the competition between the hydroxyl ions and arsenic species for adsorption sites. We selected the Zr cation for immobilization on the surface due to its stability in different pH environments. During the experiments at different pH, Zr ions were not released from the coated peels into the aqueous solution.

3.3. Isotherm Studies. *3.3.1. Langmuir Isotherm.* The Langmuir isotherm which has been commonly used for describing adsorption processes can be used to explain the adsorption of pollutants on apple peel. The basic assumption of the Langmuir theory is that adsorption takes place at specific sites within the adsorbent.[33−35] The data obtained from the adsorption experiment for different pollutants were analyzed using the isotherm equation. The saturation monolayer can be expressed by the equation.[35]

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{Kq_mC_e} \tag{3}$$

$$q_e = \frac{Kq_mC_e}{1 + q_mC_e} \tag{4}$$

A plot of $1/q_e$ versus $1/C_e$ results in a linear graphical relation indicating the applicability of the Langmuir model for different anions is shown in Figure 5a. The Langmuir constants are

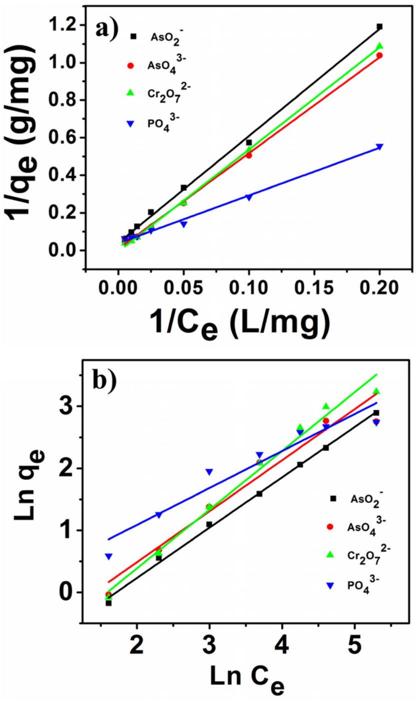

Figure 5. Langmuir (a) and Freundlich (b) isotherms for anions adsorption.

elucidated from the slope and intercept of straight lines for different anions. The observed linear relationship is statistically significant as evidenced by the R^2 values (close to unity), implying the applicability of isotherm for our extraction studies. Adsorption data for $Cr_2O_7^{2-}$ fits well with the Langmuir linear equation with the best R^2 value (0.999) compared with the others. The Langmuir isotherm constants along with correction coefficients are reported in Table 1. The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter, such as the separation factor (R_L) used in the following equation[35]

$$R_L = \frac{1}{1 + KC_e} \tag{5}$$

where K is the Langmuir constant and C_e is the initial concentration of the adsorbate in solution. This parameter indicates that the isotherm will be shaped according to the following adsorption characteristics: $R_L > 1$ is unfavorable; $R_L = 1$ corresponds to linear; $0 < R_L < 1$ is favorable, and $R_L = 0$ is irreversible. The R_L values for AsO_2^- (0.4138), AsO_4^{3-} (0.7578), $Cr_2O_7^{2-}$ (0.8294), and PO_4^{3-} (0.2468) indicate that the adsorption of anionic pollutants on to treated apple peel is favorable (Table 1).

3.3.2. Freundlich Isotherm. The Freundlich model is an empirical equation based on adsorption on heterogeneous surfaces. It is assumed that the stronger binding sites are occupied first and the binding affinity decreases with an increasing degree of site occupation.[36,37] The isotherm is expressed as

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{6}$$

where K_f and n are Freundlich constants related to sorption capacity and sorption intensity of the adsorbent, respectively. K_f can be defined as the adsorption coefficient and represents the quantity of pollutant adsorbed onto treated apple peel for a unit equilibrium concentration. A value for $1/n$ below 1 refers to a normal Langmuir isotherm while $1/n$ above 1 represents a cooperative adsorption. The $1/n$ value for AsO_2^- (0.8124), AsO_4^{3-} (0.8233), $Cr_2O_7^{2-}$ (0.9475), and PO_4^{3-} (0.5966) indicates that the adsorption follows the Freundlich isotherm. This isotherm model (Figure 5b, Table 1) also yielded good fit with the highest R^2 values for anionic pollutants, which indicates that the adsorption of anions on apple peel surface is a heterogeneous process. Table 1 lists the comparison of Langmuir and Freundlich constants for various pollutants on treated apple peel surface. It can be seen from the table that the Langmuir model was found to fit the data significantly better, indicating monolayer adsorption of anions on apple peel.

3.4. Adsorption Kinetics. Kinetic models elucidating the mechanism by which pollutants are adsorbed on adsorbent surfaces have been proposed.[38−40] Different adsorption kinetic models were used to investigate the adsorption mechanism. A pseudo-first-order eq 7 was used for data analysis;[39]

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{7}$$

where q_e and q_t indicate the amount of pollutant adsorbed (mg/g) at equilibrium and in time t, respectively. $k_1(\text{min}^{-1})$ is the first order rate constant applied in the present studies of pollutant adsorption. The plot of $\log(q_e - q_t)$ versus t for different pollutants (Figure 6a) gave first order rate constants k_1 (slope) and equilibrium concentration q_e (intercept). The values of k_1 and q_e for different pollutants were calculated from the plots and are shown in Table 2. The adsorption kinetics of some systems can also be explained by a pseudo-second-order reaction (Figure 6b). The pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form,[40]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{8}$$

where k_2 is the rate constant of pseudo-second-order adsorption and q_e is the equilibrium adsorption capacity

Table 1. Langmuir and Freundlich Isotherm Model Constants and Correlation Coefficients for Adsorption of Different Anions on Zr Immobilized Apple Peel Surface

	Langmuir			Freundlich		
pollutant	K (L/g)	R_L	R^2	K_F (mg/g)(L/g)^n	$1/n$	R^2
AsO_2^-	0.0070	0.4138	0.9973	0.2484	0.8124	0.9968
AsO_4^{3-}	0.0015	0.7578	0.9976	0.3136	0.8233	0.9362
$Cr_2O_7^{2-}$	0.0010	0.8294	0.9992	0.2216	0.9475	0.9824
PO_4^{3-}	0.0152	0.2468	0.9941	0.9007	0.5966	0.9141

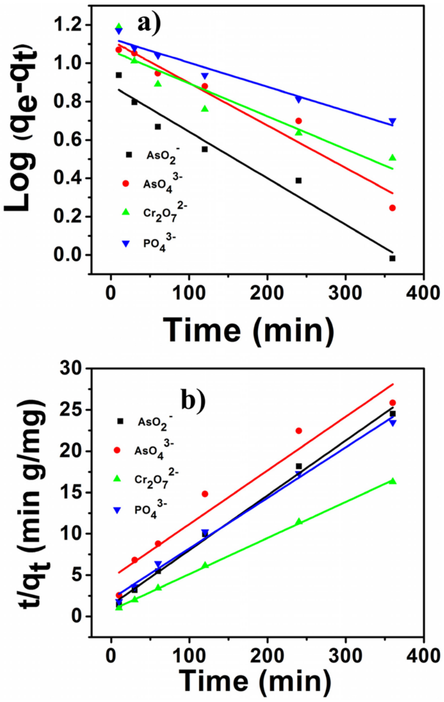

Figure 6. Pseudo-first-order (a) and pseudo-second-order (b) kinetics for the adsorption of anions onto the Zr treated apple peel.

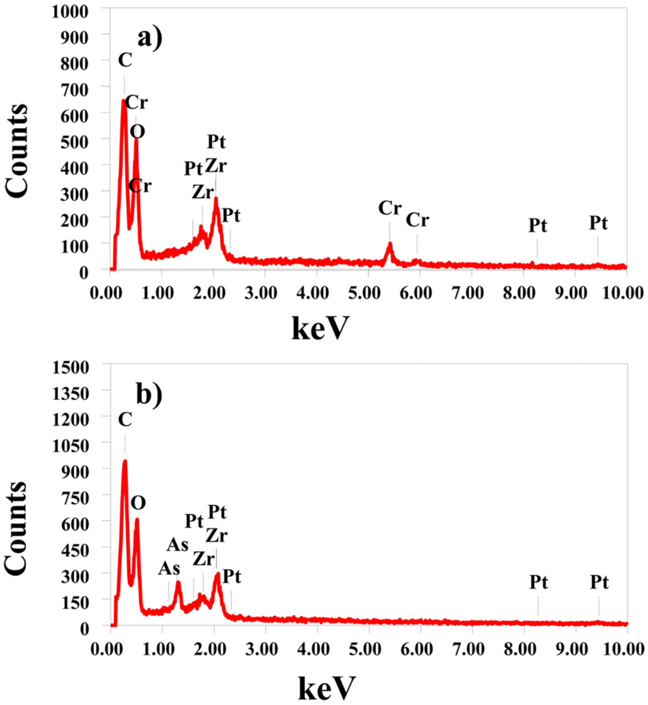

Figure 7. EDS analysis of Zr treated apple peel surface after adsorption of chromate (a) and arsenate (b) anions.

(mg/g). The k_2 and q_e values of different pollutants can be calculated experimentally from the slope and the intercept of t/q_t versus t plots. From Table 2, the correlation coefficients R^2 for AsO_2^- (0.9937), AsO_4^{3-} (0.9318), $Cr_2O_7^{2-}$(0.9990), and PO_4^{3-}(0.9990) indicate that the pseudo-second-order model fits the experimental data better than the pseudo-first-order model. The calculated correlations are closer to unity for the second-order kinetics model and calculated equilibrium adsorption capacities of all pollutants matched with experimental values. The calculated k_2 (g/mg min) and q_e are listed in Table 2.

3.5. Regeneration of Adsorbent. The adsorption of different anions on the surface of Zr treated apple peel can be confirmed by the energy dispersive X-ray spectroscopy (EDS) analysis after adsorption. The adsorbent was washed with deionized water to remove free anions after adsorption and dried at room temperature. The peels were analyzed using EDS (Figure 7), and the peaks corresponding to Cr and As were seen in the spectra along with Zr, which confirms the binding of anions on the surface of Zr treated apple peel. Mechanism of adsorption can be further investigated by using the desorption and regeneration process. The nature of the adsorption of pollutant onto the surface of the peels involves electrostatic attractions between anions and Zr(IV) present on the surface. Desorption of these pollutants was studied at different pH (2, 4, 7, 10, and 12) at a constant temperature of 30 °C. Minimum desorption was observed at acidic pH, but about 90% of pollutants were desorbed at pH 12 within 10 min (Figure 8).

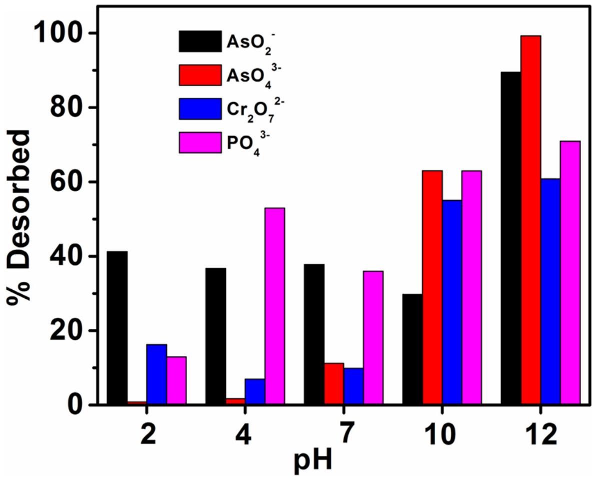

Figure 8. Desorption of anions from the Zr immobilized apple peel surface at various pH values under ambient conditions.

Table 2. Pseudo-First-Order and Pseudo-Second-Order Constants and Correlation Coefficients for Adsorption of Different Anions on Treated Apple Peel

		pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
pollutant	q_e(exp) (mg/g)	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2
AsO_2^-	15.6400	7.6749	0.0056	0.9542	15.0648	0.0032	0.9937
AsO_4^{3-}	15.6800	13.1039	0.0051	0.9451	15.3681	0.0009	0.9318
$Cr_2O_7^{2-}$	25.2860	11.6322	0.0039	0.8467	22.8676	0.0026	0.9990
PO_4^{3-}	20.3540	13.4444	0.0029	0.9533	16.3425	0.0018	0.9905

Under basic conditions, OH^- ions will replace anionic pollutants from the apple peel surface. In order to show the reusability of the adsorbent, the adsorption−desorption cycle of pollutants was repeated five times using the same experimental conditions. These results showed that recycling of treated apple peel is efficient and can be used in repeated pollutant adsorption studies without detectable losses in their adsorption capacities.

4. CONCLUSIONS

We selected Zr cations immobilized apple peel as an efficient adsorbent. Extraction of different toxic anions including chromate, phosphate, arsenate, and arsenite ions were evaluated using Zr(IV) loaded apple peel as an adsorbent. Adsorption and desorption studies were conducted to understand the adsorption mechanism. Langmuir and Freundlich isotherm models were used to validate the adsorption process. Kinetic studies were done to further understand the adsorption process, which follows pseudo-second-order kinetics. Treated apple peels showed efficient adsorption toward different anionic pollutants with experimental adsorption capacities (mg/g) of 15.64 (AsO_2^-), 15.68 (AsO_4^{3-}), 25.28 ($Cr_2O_7^{2-}$), and 20.35 (PO_4^{3-}). Experimental factors such as pH and temperature of the medium also influence the extraction efficiency. The Zr on apple peel is responsible for the extraction of different contaminants in water. It is conceivable that the use of such biowaste is a simple, cost-effective, and efficient method for water treatment and can be used in large scale applications.

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Notes

The authors declare no competing financial interest.

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