Hindawi

Research Article

Use of Green Chemistry for Amputation of Chromium Ions from Wastewater by Alkali-Treated Composts of Fruit Peels in Economical Way

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In this work, removal of chromium (VI) using alkali-treated composted peels of lemon (*Citrus limonum*), mango (*Mangifera indica)*, water melon (*Citrullus lanatus*), and melon (Cucumis melo) has been studied in batch mode. Physico-chemical characteristics of each sorbent material were determined together with their subsequent characterization by scanning electron microscopic, FTIR, and TGA. The selected sorbent materials were chemically modified using nitric acid and sodium hydroxide solutions. Adsorption efficacy of the selected sorbent materials for Cr (VI) was investigated by optimizing different parameters. The most favorable conditions were as follows: adsorbent dosage = 1.2 g/50mL, pH = 4.0, agitation speed = 170 rpm, 60 minutes = contact time, and temperature = 313°K. Base-treated adsorbents were found to be better adsorbents as compared to the acid treated form which in turn are better than raw adsorbents (adsorbents without chemical modification). Overall, the chosen sorbents removed Cr (VI) in the range of 53.62–96%, whereas the maximum sorption is with base-treated water melon peels (BWMP), that is, 95.98%. The kinetic studies discovered that the results fitted with pseudo-second-order model. Thermodynamic parameters also support that under optimal conditions, all the selected sorbents specifically base-treated sorbents are good enough for the elimination of Cr (VI) ions in an eco-friendly way.

1. Introduction

Anthropological activities have been destroying the environment since ancient times. Different factors, which deteriorated the environment, must include discharge of industrial and domestic effluents, smoke due to combustion of domestic waste materials, and vehicle fuels, domestic, and industrial sludge. Salts of different metal ions are widely used chemicals in various industrial processes. These salts are the ionic compounds and readily dissociate into their constituent ions, contributing different toxic heavy metals into water/aqueous media. Cr (VI) as many of them is reported to be having carcinogenic and nonbiodegradable nature [1]. So, a range of economical, viable, and rapid research methods is required for the elimination of these toxic substances up to their safe limits set by WHO or EPA (0.1 ppm for chromium) [2]. Toxicity of heavy metals is known to possess physical sufferings [3, 4] and also some diseases leading to

mortality [5, 6]. Various methods are available in the literature including electro-coagulation, cementation, electrodialysis, reverse osmosis, ion exchange, coagulation, precipitation, and adsorption to remove these metal pollutants from aqueous system, [7] but due to sludge formation, cost, and special need of labor, they are avoided. Adsorption got special attention as the most effective, eco-friendly, promising, and robust removal technique [8].

The salient features of adsorption process are its operational flexibility, awesomely simple unit operations, fully functional, complete regeneration, and reuse of the adsorbent [9, 10]. Adsorption of metal ions by biowaste materials involves physical or chemical phenomenon. There is electrostatic force of attraction or London–van der Waals forces between adsorbent and adsorbate in physio-sorption, whereas covalent or ionic bonding involves in chemisorption. Biosorption is a cost-effective, harmless for health and environment friendly as compared to other techniques. The conventional techniques are rendered to be comparatively inefficient, expensive, and nonspecific [11].

Pakistan produces agricultural waste residues in a large amount because it is an agricultural country, so the dumping off this waste material is a big concern in our country. In order to address this disposal issue in safer and cleaner way, agro-waste materials were selected for this study that are peels of lemon, mango, water melon, and musk melon. These fruits are consumed on large scale during summer because of semiarid, hot climate in several regions of the country to combat heating effects of hot weather on human body in natural way. In this work, it is tried to find the possibility of these peels as an adsorbent for Cr (VI) from synthetic water samples as well as industrial waste waters. Cr (VI) is largely found in tannery wastewater near to Kasur and adjacent areas of Lahore (Pakistan). Base-treated agro-waste has more removal capacity for Cr (VI), found in this work. As such, its reason and working conditions were explored in this work so that this process can be applied on macrolevel water treatment.

2. Experimental Work

2.1. Collection and Preparation of Sorbents.
Sorbent materials were selected on the basis of their abundance, easy availability, and uselessness after juice extraction. Peels of the selected fruits were collected from different juice and fruit shops of Lahore. The collected peels were washed, air-dried under shade on filter paper sheets, ground, and sieved separately. Each powdered adsorbent sample was saved in plastic bags until further use.

2.2. Pretreatments of Biomasses.
Chemical treatment of each biosorbent was done with sodium hydroxide and nitric acid by shaking 10.0 g of each adsorbent in 100 mL of acid or basic solutions for two hours. Physical treatment of individual biomasses (10.0 g) involved their autoclaving in 100 mL water for 15 min and then boiling for 10 min. All the chemically and physically treated samples were kept at 30°C in electric oven for drying and saved in air-tight glass jars after grinding with pestle and mortar [12].

2.3. Characterization of Biosorbents.
The selected biosorbents were characterized by using CHN analyzer (Exeter CE-440 Elemental Analyzer). Surface morphology was studied by SEM (JEOL model 2300 SEM) and thermal stability by thermos-gravimetric analysis (PerkinElmer Diamond Series unit, USA). FTIR spectra (PerkinElmer 1600 spectrophotometer) were used for the identification of functional groups present in biosorbents [13].

2.4. Adsorption Experiment and Preparation of Synthetic Wastewater Samples.
In order to find out the adsorption capacity of selected biosorbents for Cr (VI), AAS (PerkinElmer AA analyst 100) was used. For this purpose, synthetic water samples of known concentration were prepared in laboratory [14]. So, stock solution (1000 ppm) of K_2CrO_4 (0.37 g in 100 mL of water) was made ready and successive dilutions were done for further preparation of 10 to 50 ppm standard solutions [15].

The study of the effect of different factors such as temperature (275–375°K), contact time (10 to 120 mins), adsorbate concentration (10 to 100 mg/L), pH (1 to 7), and adsorbent dose (0.2 to 2.5 g/50mL) on whole sorption process has been done by performing batch experiments. These batch experiments were conducted at room temperature for each factor so that optimum experimental conditions could be defined for adsorption method. These experiments were performed with 50 mL of solute solution in 250-mL conical flasks at 200 rpm agitation speed on orbital shaker for 30 min. The sample solution was centrifuged after shaking and filtration, and remaining concentration of Cr (VI) in the filtrate was determined by AAS. The experiments were replicated three times. Following equations were used to calculate the amount of Cr (VI) ions adsorbed onto selected sorbents at equilibrium (qe) and the percentage of Cr (VI) removal:

$$qe = \frac{(Co - Ce)V}{M}, \tag{1}$$

$$\%\text{removal} = \frac{(Co - Ce) * 100}{Co}. \tag{2}$$

where Co is initial concentration of adsorbate solution (mg/L), Ce is equilibrium concentration of adsorbate solution (mg/L), V is volume (L) of adsorbate solution, and M is adsorbent mass (g).

2.5. Optimization of Adsorption Parameters.
The adsorption capacity of different biomasses for chromium ions is mainly dependent on the nature of interaction between sorbent and the sorbate [16]. This sorbent-sorbate interaction is further correlated with the chemical composition and surface morphology of the sorbent as well as on the behavior of metal ion in water samples. Optimization of various parameters, such as time of contact, metal ion concentration, sorbent dose, pH, and temperature of medium, is necessary for the study of adsorption phenomenon in batch mode [17].

2.5.1. Effect of pH. Optimization of pH has been done in the range of 1 to 7 while keeping the other parameters constant, that is, 2 g of the sorbent dose per 50 ml of 50 ppm sorbate solution at 100 rpm speed for 30 min at 30°C.

2.5.2. Effect of Sorbent Dose. Sorbent dose was optimized by varying the sorbent amount from 0.2 to 2 g per 50 mL of 50 ppm of sorbate solution at constant temperature (30°C), shaking speed (50 rpm), shaking time (30 min), and constant pH (4).

2.5.3. Effect of Contact Time. After optimizing the sorbent dose (1.2 g/50 mL of sorbate solution) and pH, that is, 4, time of contact was optimized by keeping the remaining factors constant including temperature and shaking speed.

2.5.4. Effect of Cr (VI) Concentration. Optimization of metal ion concentration was done by varying its concentration in the range of 10 to 50 ppm while keeping all the other parameters at fixed optimized values [18].

2.5.5. Effect of Temperature. Consequences of temperature effect on sorption phenomenon were found out by keeping all the other factors at optimized values and changing the temperature values in the range of 275–375°K.

2.6. Kinetic Studies. The optimization data were interpreted by employing the pseudo-first-order and pseudo–second-order kinetic models mentioned in following equations:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}. \tag{4}$$

2.7. Thermodynamic Studies. To find different thermodynamic variables, that is, entropy (ΔS^o), enthalpy (ΔH^o), and Gibb's free energy (ΔG^o) [19], the graph of $\log(q_e/C_e)$ *vs* 1/T was employed to compute the value of ΔS^o from intercept and that of ΔH^o from slope through Microsoft Excel 2010. ΔG^o was computed from following equations:

$$\Delta G^o = \Delta H^0 - T\Delta S^0, \tag{5}$$

$$\Delta G^0 = RT \ln K_D, \tag{6}$$

$$K_D = \frac{C_o - C_e}{C_e}, \tag{7}$$

$$\ln K_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}. \tag{8}$$

2.8. Effect of Ionic Strength of Interfering Salts. The effect of interfering salt on the removal efficiency of selected sorbents was studied according to a reported procedure [20].

2.9. Statistical Analysis. The results of experiments were calculated as mean of experimental sets with standard deviations. Thermodynamics equilibrium and kinetics coefficients were found by applying regression techniques [21].

3. Results and Discussion

In the present study, adsorption of Cr (VI) ions was monitored and determined on the peels of four fruits, that is, lemon, mango, melon, and watermelon. The sorbent materials were selected on the base of their plentiful disposal as agro-waste materials, which are just discarded after extracting the juice [22]. These waste materials create sanitation problems as well as their intrusive odor contaminate the environment if it is left over for some time because the common methods of disposal of these waste materials are the dumping off in some landfills or burnt to fire. So, this waste material can be used for a good purpose like adsorption to make the environment clean rather than polluting the environment by just discarding it [23].

Prior to the study of sorption efficiency of these peels, their surface was characterized to investigate their chemical composition and surface morphology because adsorption is surface phenomenon and surface chemical composition is responsible for binding nature of sorbate particles on the surface of sorbent materials [24].

3.1. Characterization of Sorbent

3.1.1. Proximate Analysis. Reported method was employed for the proximate analysis of the four sorbent materials under study [25]. The selected sorbent materials were analyzed, and the percentage values of cellulose, hemicellulose, lignin, and fiber were tabulated in Table 1. The selected sorbent materials are analyzed to find out the percentage of lignin, fiber, hemicellulose, and cellulose. It was found that all the four sorbents had high contents of cellulose, fiber, hemicellulose, and lignin.

3.1.2. Elemental Analysis. Elemental analyzer was used to find out the percentage values of H, C, and N in raw biosorbents, and the findings were tabulated in Table 2. According to the findings, the presence of high carbon contents in all the four biowaste materials revealed their substantial potential as biosorbents. Efficiency of a sorbent material for the removal of sorbates of varying chemistry, that is, polarity, from its surface is strongly influenced by content of carbon. Carbon content, upon burning, gives activated carbon, which has very established removal efficiency.

3.1.3. FTIR Spectroscopic Analysis. FTIR is a state-of-the-art analysis technique for the identification of different functional groups, which in turn characterize any synthetic or natural material.

TABLE 1: Physicochemical analysis of sorbent materials.

Sorbents	Moisture (%)	Volatile matter (%)	Ash (%)	Fixed carbon (%)	Fiber (%)	Lignin (%)	Cellulose (%)	Hemicellulose (%)
Lemon peel (LP)	8.73	5.15	84.97	1.15	37	22	16	5
Melon peel (MP)	8.16	6.85	84.01	1.03	33	24	15	4
Water melon peel (WMP)	6.36	4.71	88.43	0.50	32	25	21	11
Mango peel (MnP)	9.72	4.12	84.53	1.63	38	23	13	6

TABLE 2: Percentage (%) of carbon, hydrogen, and nitrogen content in sorbent materials.

Sorbent	C	H	N
Lemon peel (LP)	33.35–36.56	5.29–7.34	1.25–3.36
Melon peel (MP)	28.89–30.33	4.47–6.25	1.23–2.49
Water melon peel (WMP)	26.13–29.09	7.11–7.92	2.56–4.32
Mango peel (MnP)	36.10–38.34	3.31–5.43	1.24–3.34

The presence or absence of a functional group in a material gives information about its structure and its properties. Among all the samples, WMP was found to be the most potential sorbent; therefore, its FTIR spectra were also recorded by treating raw WMP sample with 0.1 N nitric acid and 0.1 N sodium hydroxide separately to note the shifting of absorption bands in comparison with IR spectra of raw material [12].

Normally carboxylic, phenolic, hydroxyl, alkanes, aromatic groups, amines, and alkyl groups are detected by FTIR spectra in the peels of different sorbent materials. FTIR spectra of all the sorbents (Figure 1) were matching for significant wavenumber range [26], which suggests the presence of same functional groups mainly in all the sorbent materials, although quantitatively significant variation is observed. Very complex mixture of peaks was obtained around or above 3500 cm^{-1} in FTIR spectra of all the sorbent materials, but in case of WMP, the FTIR data revealed the presence of –NH or –OH groups as indicated by the deep band around 3100 cm^{-1} in IR spectra. The base-treated adsorbents showed deeper band in the aforementioned range, which may be due to the increased concentration of –OH groups upon basic treatment of selected sorbents [26]. In LP, MnP, and MP, one set of peaks was also found between 2900 and 2800 cm^{-1}, which may be linked with the stretching of O-H of -COOH group and its bending vibrations were recorded near 1400 cm^{-1}. A wide range of fused type peaks was found in the region of 1400–900 cm^{-1} [27]. These peaks may be the indication of complex matrix. There were also peaks at 1049.71, 1230.82, and 795.97 cm^{-1} indicating the presence of C-O stretch, phenol/tertiary alcohol, and primary amine and C-N stretch, respectively [28].

The presence of methylene, methoxy, and methyl group was identified due to the peaks observed near 2900 cm^{-1} in different spectra, which are the stretching frequency of the C-H bonds. An intense peak in spectrum of WMP, at 1000–1031 cm^{-1}, is due to the alcoholic or carboxylic C-O bond stretching.

3.1.4. SEM Analysis.
Morphological characterization and surface texture determination of the raw sorbents were done via SEM analysis for the assessment of their sorption potential for the removal of chromium ions. Scanning electron micrographs are presented as Figures 2(a)–2(d) for LP, MP, WMP, and MP, respectively. SEM graphs reveal the presence of different sized pores with different depths on the surfaces of all the sorbent materials. Apparently, the micrographs of WMP are showing pores of irregular shapes [29], while in SEM graph of LP, there is uniform distribution of pores over surface. It may be hypothesized that the pores of irregular shape on WMP are responsible for the effective binding with different sorbate materials, while LP might have least adsorption [30].

3.1.5. Thermogravimetric Analysis.
Thermogravimetric analysis provides information about thermal decomposition pattern of materials under investigation and effectively examines the chemical changes pattern in the lingo-cellulose matter. Hemicellulose, being highly unstable compound, decomposes first followed by lignin and cellulose [31, 32]. Four raw sorbent materials, that is, LP, MP, WMP, and MnP, were subjected to thermogravimetric analysis, and decomposition pattern of each material was noted (Figure 3). Recorded thermo-grams revealed that almost all the sorbents exhibited the decomposition in three stages. The initial weight loss below 200°C may be due to the loss of water type in low volatile matter. In next step, the weight loss in the range of 200–400°C may be the result of lignin and cellulose breakdown. These two components pyrolyze into monomeric phenols, aromatic rings, and pyranose structures [33]. The slow decomposition of heavy components to their respective metal oxides was noticed above 500°C due to a continuity in weight loss [26].

3.2. Adsorption Parameters.
As the adsorption is a surface phenomenon, so it is dependent on the physical or chemical interaction of the sorbent and the sorbate particles. Efficiency of sorption process depends on nature of binding forces between sorbent and sorbate, which in turn is dependent on number of factors. Optimization of different parameters such as agitation speed, pH, and temperature was necessary for the effective removal of sorbate particles.

Removal efficiency of four sorbent materials, chosen for this study, that is, LP, MP, MnP, and WMP, was studied by optimizing the above-mentioned parameters to achieve the maximum removal of Cr (VI) ions. In order to improve the adsorption capacity of these sorbent materials, each was treated chemically with acid (0.1N HNO$_3$) as well as base (0.1N NaOH). Furthermore, all the 3 forms of sorbents, that is, the raw sorbent, its basic, and acidic treated forms, were
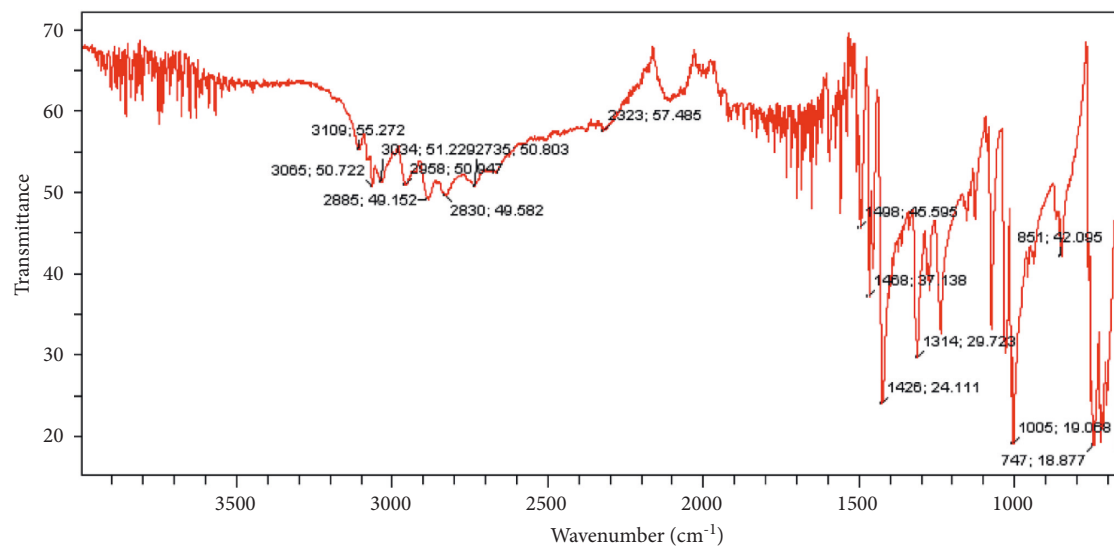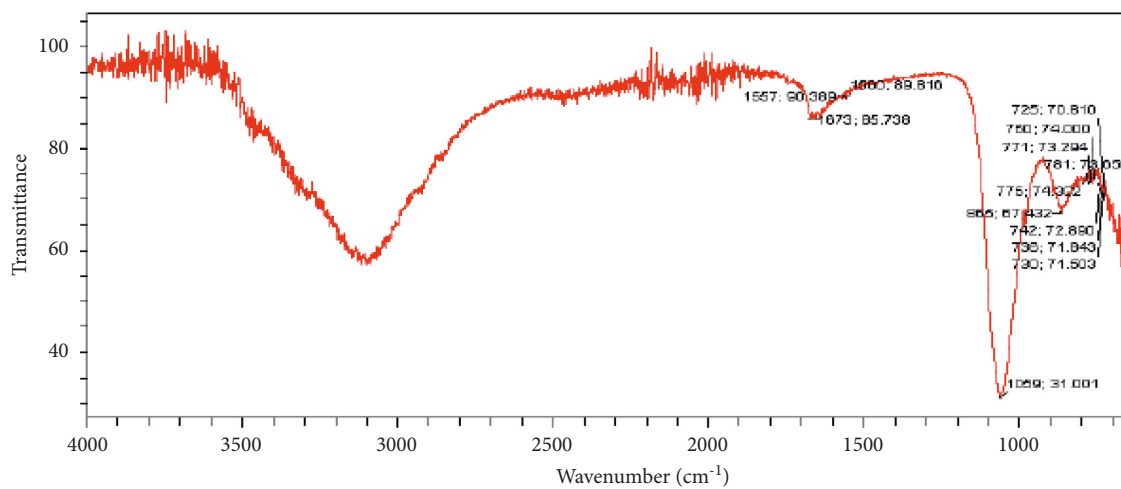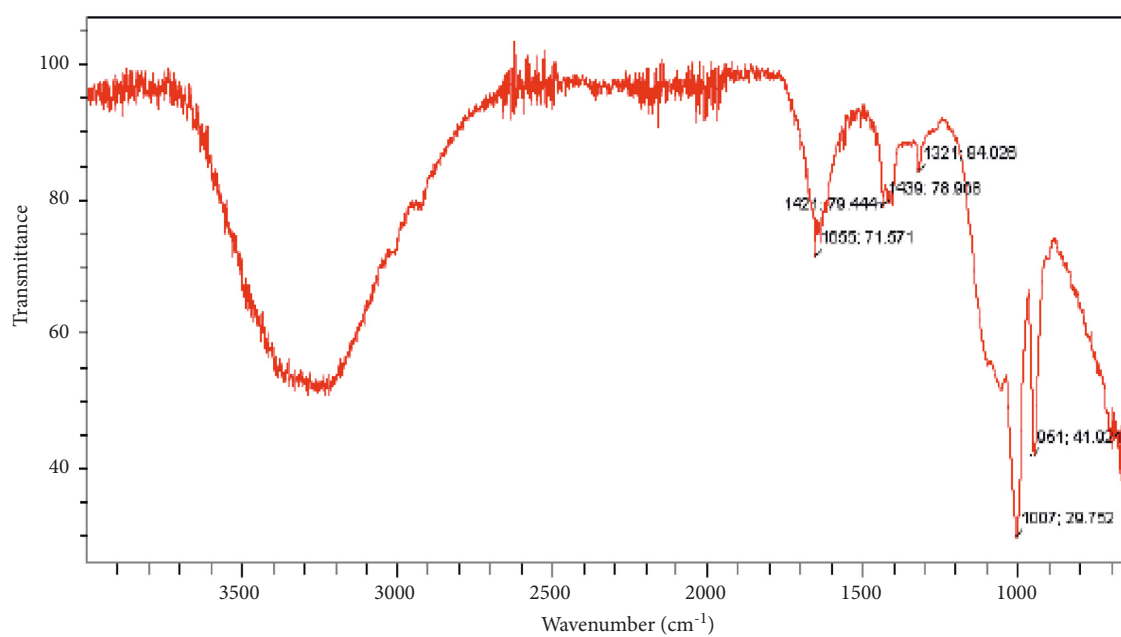
(a)
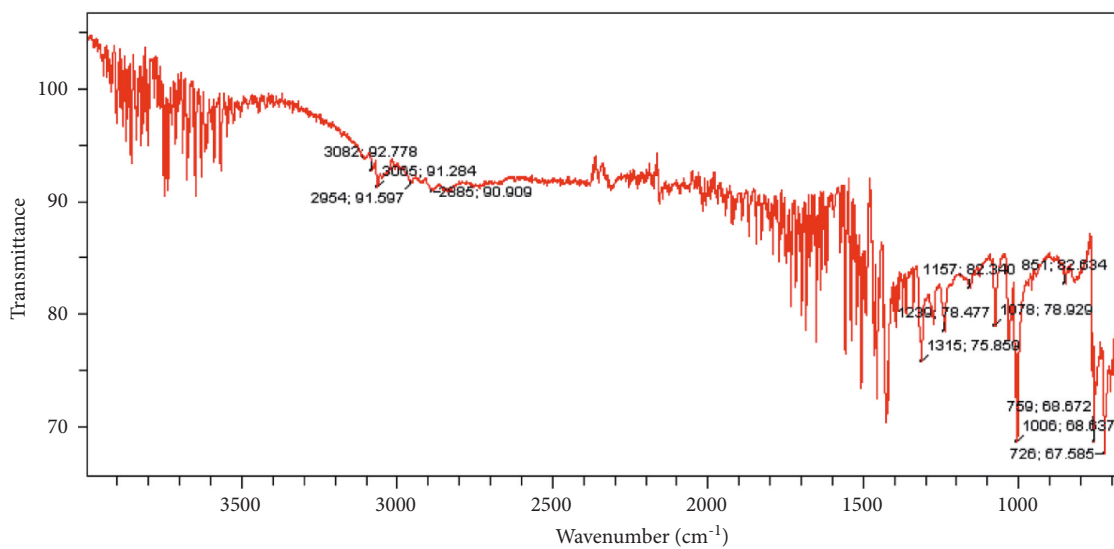
(b)
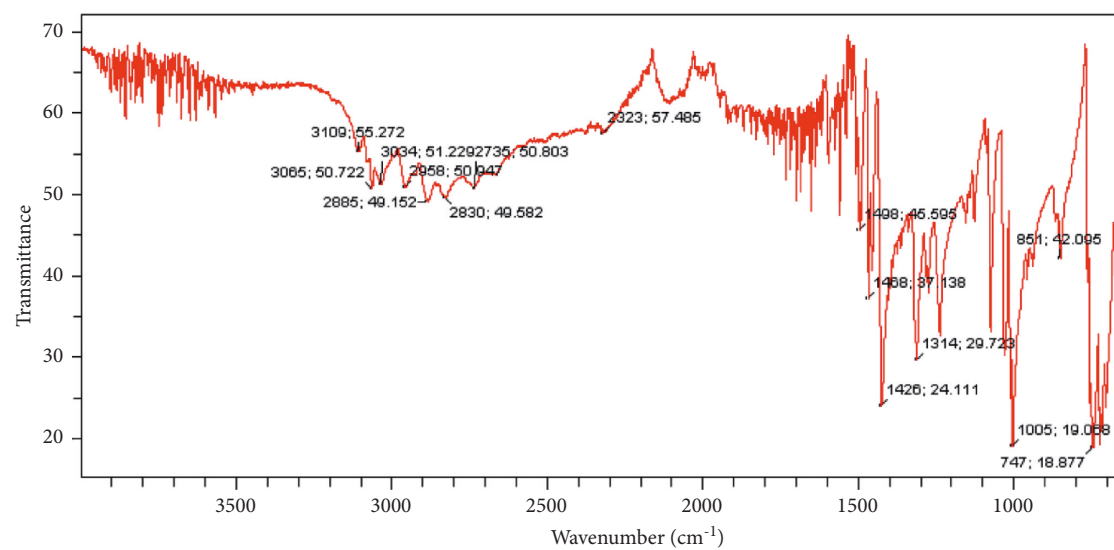
(c)

FIGURE 1: Continued.
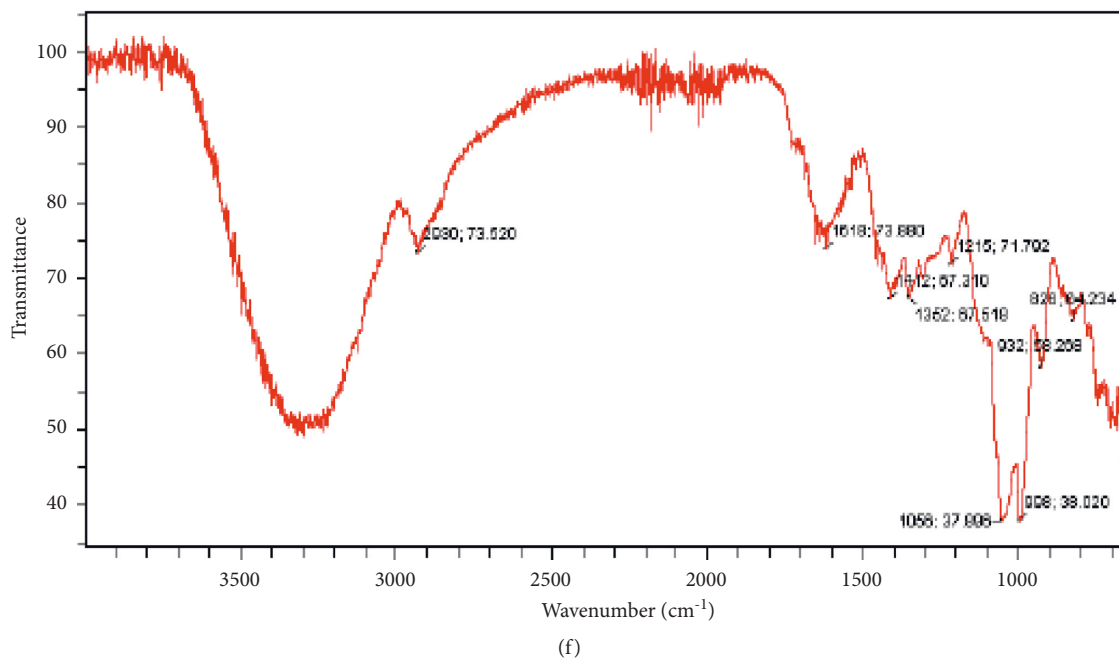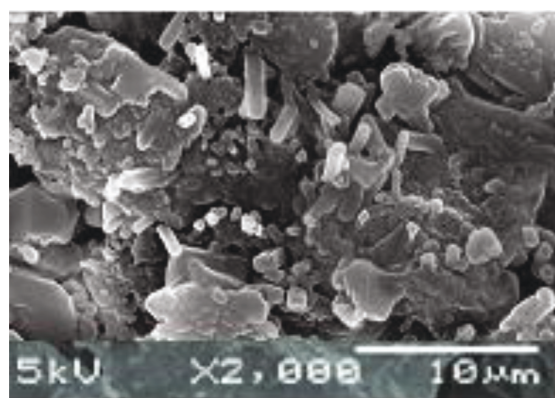
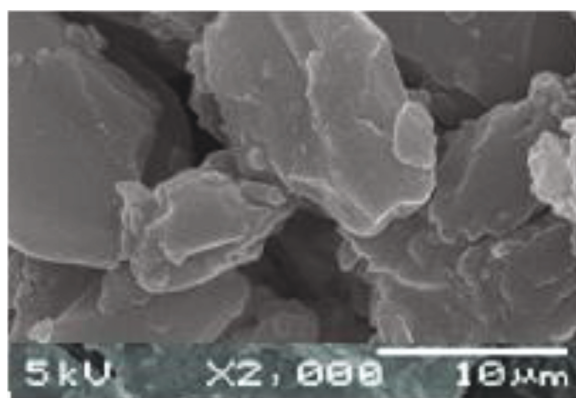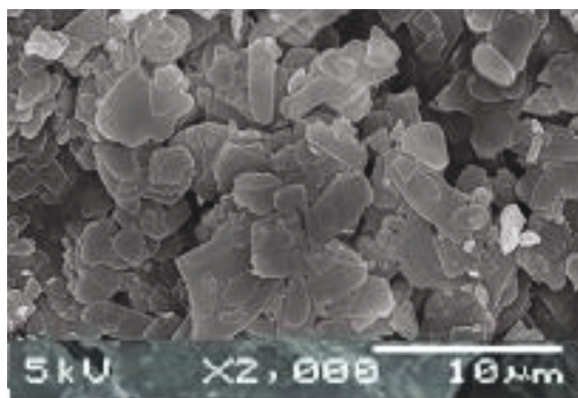(d)

(e)

FIGURE 1: Continued.

(f)

FIGURE 1: FTIR spectra of (a) LP, (b) MP, (c) WMP, (d) MnP, (e) A-WMP, and (f) BWMP.
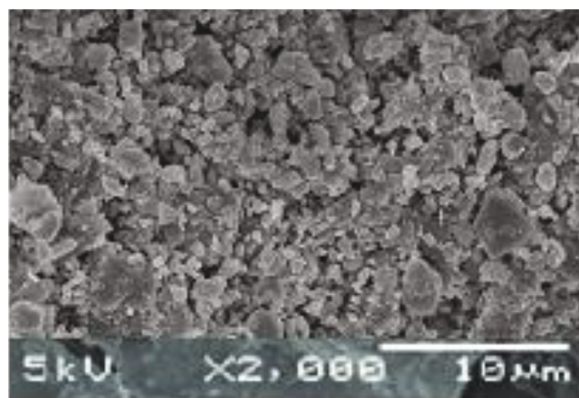

(a)

(b)

(c)

(d)

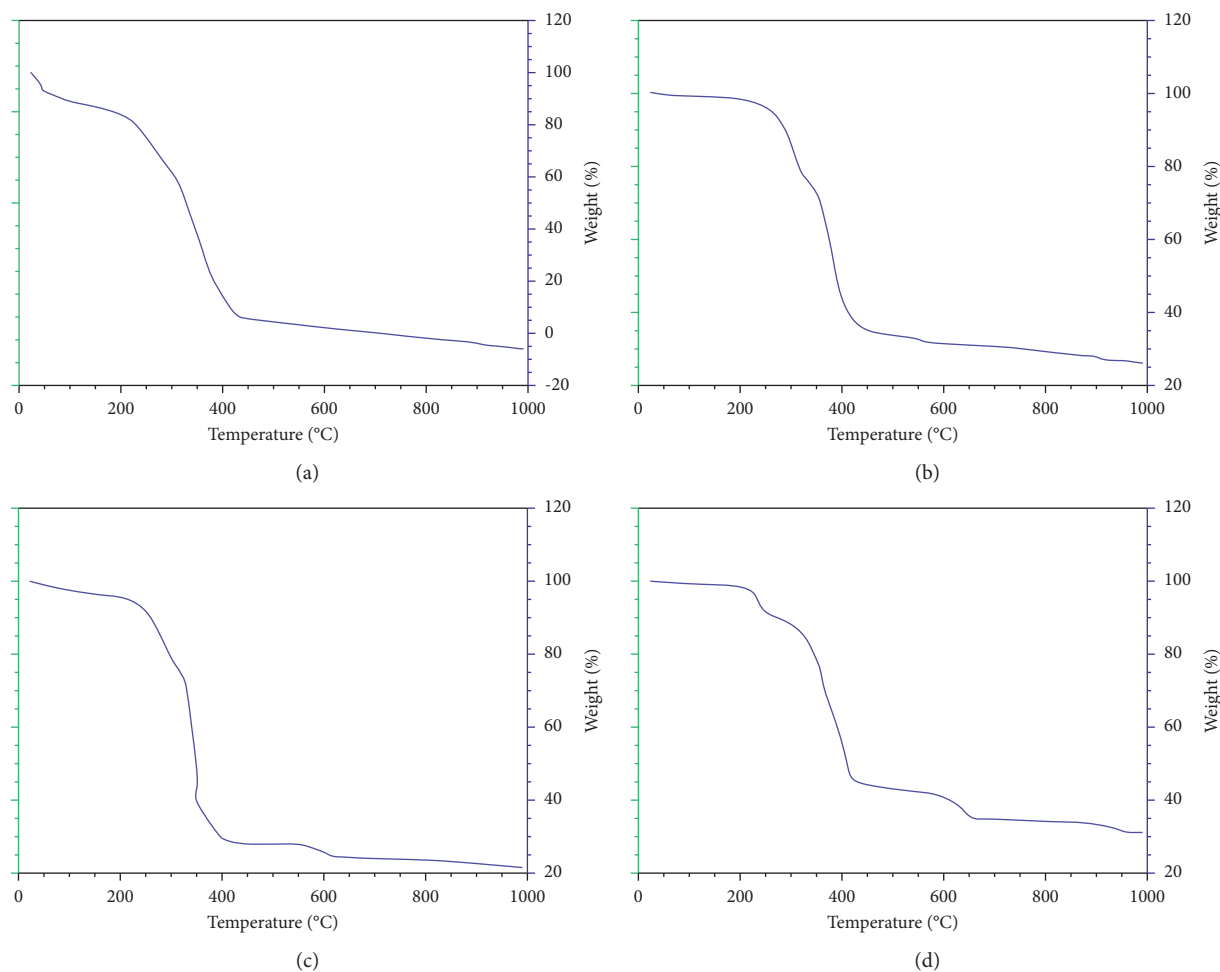FIGURE 2: SEM micrograph of (a) LP, (b) MP, (c) WMP, and (d) MnP.

FIGURE 3: TGA curve for (a) LP, (b) MP, (c) WMP, and (d) MnP.

verified for the adsorption of sorbate particles, that is, chromium (VI). Optimization of each parameter is described as follows:

3.2.1. Effect of Sorbent Dose.
Sorption of Cr (VI) was carried out in the range of 0.2–2.0 g with the given four different sorbents for different sorbent doses, that is, in their raw form, acid- and base-treated forms. Among the raw sorbents, base-treated sorbents, and acid-treated sorbents, maximum removal was observed for base-treated sample among all the given four types of sorbents in accordance to the previous reported data [34]. For the removal of Cr (VI), maximum removal efficiency was exhibited by BWMP at sorbent dose of 1.2 g/50 mL, which was 95.98%, while the other base-treated sorbents, that is, LP, MnP, and MP, showed the removal efficiency in the range of 80–90%. So, the increasing order of sorption of Cr (VI) with base-treated sorbents would be written as WMP > LP > MnP > MP as shown in Figure 4.

3.2.2. Effect of Contact Time.
Maximum removal of chromium ion by the selected sorbents was found in the contact time duration of 20–30 min. Among the different forms of each sorbent material, base-treated form of each sorbent exhibited the highest removal efficiency for Cr (VI), followed by acid-treated and raw forms, respectively.

This study suggested that maximum removal of Cr (VI) was achieved on base-treated WMP, that is, 90.81% in the contact time of 20 min, followed by base-treated LP and base-treated MP with the sorption values of 87.67% and 88.24% with the contact time of 20 and 35 min for Cr (VI), respectively. Similarly, for base-treated MnP, the optimized sorption was achieved in 30 min with the sorption of 86.92%. This revealed almost the same trend, as in previous step. So, the order of decrease in sorption of Cr (VI) on different base-treated sorbents is WMP > LP > MP > MnP as shown in Figure 5.

3.2.3. Effect of pH.
Degree of chelation, precipitation, and solubility of metal ions are strongly influenced with pH change. Solutions of the opted sorbate, that is, chromium ions, were prepared in aqueous buffers, having pH range of 1–7. pH above 7 could not be studied, as the sorbates form insoluble hydroxides at alkaline pH [29]. Same trend of removal efficiency was followed as previously observed. Among the different forms of each sorbent, base-treated materials showed relatively higher removal efficiency, and overall, base-treated WMP exhibited the highest removal
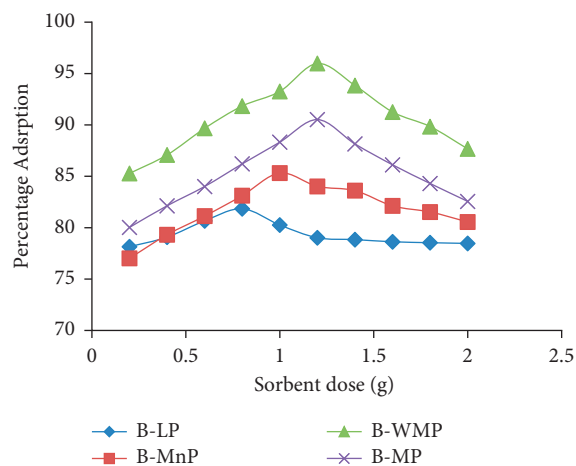
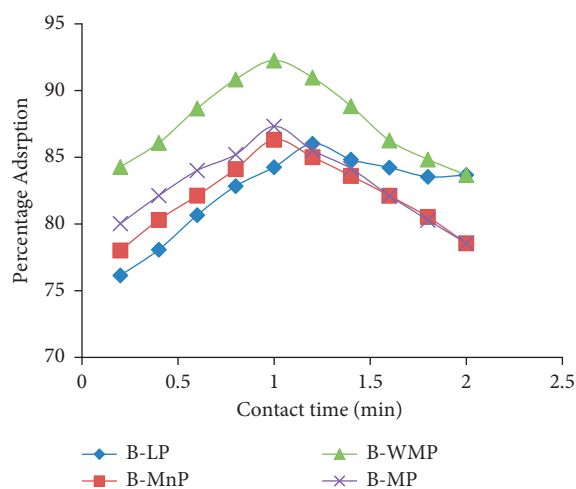FIGURE 4: Effect of sorbent dose on the sorption of Cr (VI).

FIGURE 6: Effect of pH on the sorption of Cr (VI) on different sorbents.

FIGURE 5: Effect of contact time of different sorbents on the sorption of Cr (VI).
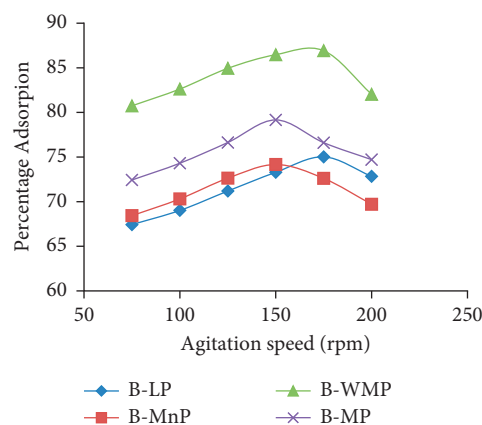
FIGURE 7: Effect of agitation speed on the sorption of Cr (VI) on different sorbents.

efficiency for Cr (VI). The maximum removal range was observed in the range of 2–4 pH, while raw forms of all sorbents exhibited maximum sorption at pH 5. For base-treated WMP, the maximum sorption was achieved at pH of 4, that is, 91.08%, while B-LP at pH 4 and B-MP at pH 3 showed sorption 79.26% and 80.60%, respectively. Supreme pH for B-MnP was found to be 3 with the sorption of 85.85%. So, the decreasing order of the sorption of Cr (VI) for all the above-mentioned base-treated sorbents is WMP > MnP > MP > LP (Figure 6).

3.2.4. Effect of Agitation Speed. Sorbate samples are soaked at particular agitation speed, and adsorption capacity was monitored. As agitation increases, the available surface area for Cr (VI) ions enhanced and distributes effectively in solutions. It avoids buildup of particles at any particular place in solution, hence ensures the smooth placement of sorbates onto the surface of sorbent until establishment of equilibrium. A range of 75–200 rpm was chosen for the
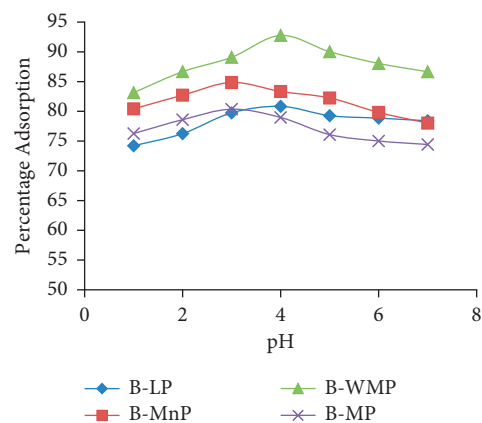
optimization of agitation speed. Maximum removal was achieved at speed of 125–200 rpm. The minimum sorption was observed on raw LP at 200 rpm, which was 68.29%. Here again, the base-treated sorbents showed significantly high sorption capacity for Cr (VI). The maximum sorption was achieved by the BWMP at a 170 rpm, that is, 88.47%. Overall, the decreasing order of the sorption of Cr (VI) for all the selected base-treated sorbents at different agitation speed is as follows: WMP > MP > LP > MnP (Figure 7).

3.2.5. Effect of Temperature. Temperature significantly influences the magnitude as well as the rate of adsorption. Sorbate-sorbent interaction was studied by varying the temperature of solution over range of 275–375°K. For the observation of the effect of temperature on process of sorption, again raw sorbents, acid-treated and base-treated sorbents were employed. Maximum removal of Cr (VI) was done by base-treated sorbents. Minimum sorption was observed on raw MnP, that is, 64.02% at 283°K, while the maximum sorption of Cr (VI) was showed by B-MP at 323°K, which was 90.26%. In case of BWMP, the achieved sorption was 85.68% at a

FIGURE 8: Effect of temperature on the sorption of Cr (VI) on different sorbents.
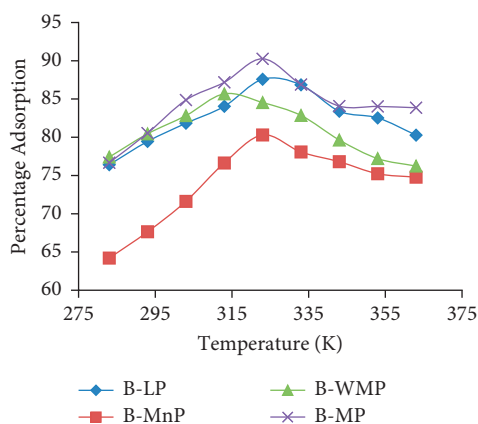
TABLE 3: Langmuir isotherm for Cr (VI) removal by base-treated sorbents.

Sorbents	Slope	Intercept	R^2	q_m (mg/g)	B (L/g)	Specific surface area (m^2/g)	Separation factor R_L
BLP	5.93	0.050	0.979	20.41	0.011	6.07	0.707
BMnP	2.1	0.047	0.994	22.56	0.020	6.61	0.531
BWMP	2.59	0.038	0.971	30.93	0.021	6.21	0.523
BMP	3.12	0.041	0.963	25.77	0.019	5.18	0.596

TABLE 4: Freundlich isotherm for Cr (VI) removal by base-treated sorbents.

Sorbents	Slope	Intercept	R^2	K_F (mg$^{1-1/n}$L$^{1/n}$g^{-1})	n
BLP	0.410	0.105	0.981	0.790	2.45
BMnP	0.400	-0.280	0.965	0.522	2.52
BWMP	0.180	0.297	0.893	1.981	5.72
BMP	0.332	-0.188	0.970	0.650	3.04

temperature of 313°K. So, the concluded decreasing order of the sorption with the base-treated sorbents is MP > LP > WMP > MnP (Figure 8).

3.3. Mathematical Modeling

3.3.1. Isothermal Studies. Modeling of equilibrium data is quite important step for the industrial application of sorption, as it helps in comparing various material efficiencies [35]. Here, Langmuir and Freundlich models were used. From all the samples, base-treated sorbents show best results for Cr (VI) at optimized conditions of operational parameters as evident from Tables 3 and 4.

For Langmuir model, the values of regression coefficient (R^2) for all base-treated sorbents are near to unity. It was presumed on the basis of R^2 values that Langmuir model was followed in this case. Tabulated values (Table 3) showed that the values of maximum removal capability "q_m" was maximum for base-treated water melon peel followed by melon peel > mango peel > lemon peel for the metal ion, that is, Cr (VI). Langmuir-specific surface area "S" was calculated by "q_m" values. This factor is a measurement of increment in the sorption capacity of different sorbates under study. The tabulated values showed that the specific surface area of base-treated water melon peel (BWMP) for chromium (VI)

is highest among all the sorbates. R_L for Langmuir isotherm is a dimensionless separation factor constant, which explains the suitability of sorption phenomenon. $R_L < 1$ is an indication of the suitability of sorption process on larger scale. This supports that under optimal conditions, all the base-treated sorbents are good enough for the removal of Cr (VI) ions.

Multilayer heterogeneous adsorptive removal phenomenon is described by Freundlich model, and it favors physio-sorption more. Freundlich parameter "n" predicts quality of sorption process. $n = 2–10$ shows better sorption, while $n = 0–2$ indicates good sorption [35]. As presented in Table 4, the "n" value of all sorbents under this study is in the range of 0–6. So, they are good sorbents for the chromium ions under this study. If "n" is larger, then the system is more heterogeneous resulting in nonlinearity of the isotherm. The Freundlich parameter K_F values reveal an effective bonding between chromium ions and sorbent. Base-treated water melon peel (BWMP) showed highest values of K_F for Cr (VI) followed by MP > MnP > LP. These values represent a constant partitioning of the sorption mechanism where chromium ions are penetrated in the sorbent effectively thus indicating a good sorption [36].

3.3.2. Kinetic Studies. Kinetic models are helpful in the study of reaction mechanism. Pseudo-first-order and pseudo-second-order models were applied on the obtained experimental data to determine the most suitable kinetic equation, which may predict the sorption mechanisms for opted sorbates. The coefficient (R^2) values were quite low for first-order kinetic model, indicating that this model was not applicable to our findings, whereas second-order model was found to be fit on our sorption data. Therefore, pseudo-second-order kinetic

TABLE 5: Kinetic model data for the removal of Cr (VI) by base-treated samples.

| Sorbents | Pseudo-second-order kinetics parameters | | | | | H (mg/g·min) | $t_{1/2}$ (min) |
	Slope	Intercept	R^2	K_2 (lg/mgl/min)	q_e (mg/g)		
BLP	1.191	15.55	0.908	0.081	0.79	0.065	10.17
BMnP	0.922	10.74	0.930	0.085	1.13	0.099	12.73
BWMP	0.399	4.61	0.979	0.090	2.51	0.495	27.86
BMP	0.641	7.84	0.921	0.082	1.63	0.187	19.45

model was applied in further investigations. The pseudo-second-order rate constant k_2, initial sorption rate h, amount of Cr (VI) ions at equilibrium q_e, and the corresponding correlation coefficient R^2 values are presented in Table 5. This model was successfully applicable to equilibrium data. The values of R^2 were in the range 0.908 to 0.979 thus approaching to unity for all four sorbents under this study (Table 5). These findings were in agreement with the relevant literature of sorption studies [37] and with the generally established opinion of the workers that the biosorption processes usually follow pseudo-second-order kinetics.

The values for initial sorption rate (h) are more for BWMP, which means plenty of adsorption site were available for the metal ion thus favoring good adsorption. Similarly, half adsorption time "$t_{1/2}$" follows the general trend as: BWMP > BMP > BMnP > BLP.

3.3.3. Thermodynamic Studies.
Thermodynamic parameters of a sorption phenomenon are very important to be determined in order to see whether the said process is spontaneous or nonspontaneous. These parameters have significant role to explain feasibility and heat variations of adsorption phenomenon.

Changes in Gibbs free energy, entropy, and enthalpy, that is, (ΔG^o), (ΔS^o), (ΔH^o), were calculated for the understanding of the thermodynamic properties of the sorption process of chromium ions by base-treated sorbents. Calculations were done on the basis of optimized values of pH, contact time interval, shaking speed, and adsorbent dose with variable temperature values from 10 to 90°C. The data for the values of ΔG^o, ΔH^o, and ΔS^o thus calculated are tabulated in Table 6. Gibbs free energy values obtained after calculations are negative and hence an indication of the spontaneity of the sorption process. Additionally, the ΔG^o increased with the increase in temperature, thus suggesting that sorption could be more spontaneous at lower temperature. It is reported in the literature that if the ΔGo fall in the range of 0–20 kJ/mol, it would be physio-sorption, and if they are between 80 and 400 kJ/mol, it would be chemi-sorption [29]. So, it seems that the sorption in the present study is physio-sorption as the ΔG^o values indicate the physical phenomenon during sorption process. Moreover, the negative values of enthalpy change for sorption process are an indication of exothermic process. Furthermore, ΔS^o values are showing that the randomness has been increased at the sorbent-sorbate interface during sorption process because these entropy values are positive [37]. From these parameters, overall physio-sorption process during this study is proposed.

3.4. Effect of Ionic Strength of Interfering Salts.
It is necessary to study the interference of various ions on the scavenging efficiency of the sorbent surface for the chromium ions, because different minerals are present in natural water like sulfate, chloride, phosphate, magnesium, and sodium.

A decrease in the scavenging efficacy of the sorbents takes place in the presence of 05–20 ppm solution of sodium chloride and sodium sulfate. The order of decrease in percent sorption of sorbates (100 mg/L) onto 0.2 g of water melon and melon sorbent is listed in Table 7. The decrease in the removal efficiency of the selected sorbents is not very appreciable. Hence, it is obvious that the presence of salts like sodium sulfate and sodium chloride does not show any interference on the adsorption capacity of the sorbents under study.

3.5. Applications of Developed Method to Industrial Wastewater Samples.
Contaminated surface water as well as ground water was sampled from the area near to different industries in Lahore, Pakistan. Contaminated samples for surface water were collected from various points at the canal (Lahore) nearby industrial area. Similarly, contaminated samples for ground water were collected from the hand pump placed at the same industrial area of Lahore. Water sample from hand pump was collected after flushing out approximately 50 mL of water. The process is summarized in Figure 9.

Duplicate samples for Cr (VI) measurement were collected from the sampling location in sterilized 10-L glass containers and immediately transported to the laboratory in an air-conditioned automobile and stored in a refrigerator at 4°C until further use. These samples were filtered by 0.45-μm Whatman glass filter paper to remove particulate matter. After filtration, same water samples were then spiked with 10 ppm solution of the Cr (V1). 10 μL of these spiked samples was then subjected for the quantification of metal ions in real sample water. Amount of chromium ions was found to be 3.6 μg·L^{-1} [32]. In order to study the removal efficiency of opted biosorbents, 0.2 g of these WMP, MP, MnP, and LP adsorbents was poured into four separate 250-mL Erlenmeyer flasks with stopper. 100 mL of spiked water sample was added into the same flasks and left for shaking for 1 hour following the aforementioned experimental conditions under the title of optimization studies. 10 μL was injected to instrument for the analysis by adopting sorption method stated earlier. Peels of water melon, melon, mango, and lemon efficiently eradicated chromium ions present in samples of waste

TABLE 6: Thermodynamics of base-treated peel samples for removal of Cr (VI).

| Adsorbents | Thermodynamics parameters | | | | | ΔG^{o} (kJ/mol) |
	Slope	Intercept	R^2	ΔH^{o} (kJ/mol)	ΔS^{o} (J/mol/K)	
BLP	0.002	0.002	0.987	−0.038	0.035	−10.99
BMnP	0.002	0.003	0.941	−0.054	0.037	−11.76
BWMP	0.004	0.003	0.919	−0.043	0.067	−19.64
BMP	0.003	0.002	0.945	−0.051	0.059	−17.89

TABLE 7: Influence of interfering salt NaCl/Na$_2$SO$_4$ on the sorption of Cr (VI).

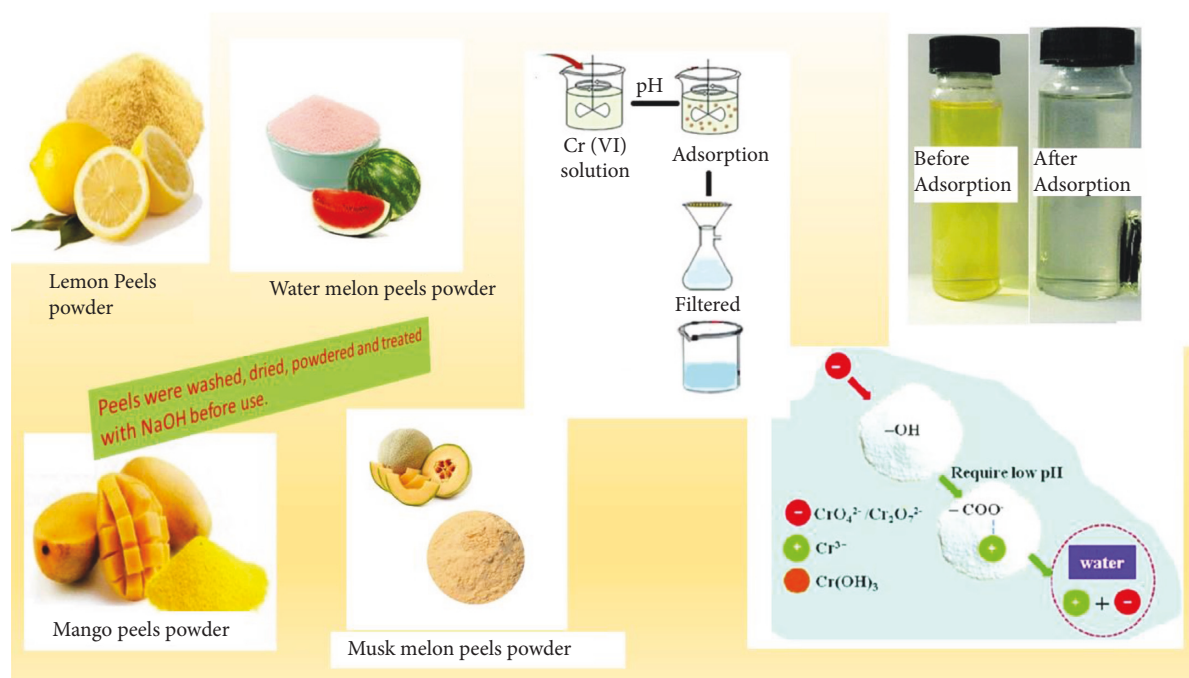| Interfering salt concentration (mg/L) | Decrease in % sorption for chromium ions | | | |
	WM	MnP	WMP	MP
20	3.82 ± 0.421	3.63 ± 0.214	2.13 ± 0.424	4.63 ± 0.814
10	2.33 ± 0.414	2.44 ± 0.232	1.56 ± 0.414	2.81 ± 0.832
05	2.63 ± 0.431	1.93 ± 0.215	1.74 ± 0.431	1.53 ± 0.828

FIGURE 9: Summarizing the scheme of process.

TABLE 8: Percent sorption and percent recoveries of Cr (VI).

| Sorbent | Surface water | | Ground water | |
	Removal* (%)	Recovery* (%) with 5 mL methanol	Removal* (%)	Recovery* (%) with 5 mL methanol
WMP	96.72 ± 0.411	96.82 ± 0.432	97.32 ± 0.413	95.32 ± 0.433
MnP	97.83 ± 0.223	94.73 ± 0.231	97.34 ± 0.247	93.21 ± 0.236
LP	96.31 ± 0.421	95.22 ± 0.414	95.21 ± 0.463	91.74 ± 0.426
MP	98.32 ± 0.861	95.73 ± 0.816	92.32 ± 0.796	92.47 ± 0.834

water. The recovery of the Cr (VI) ions that is sorbed on the surface of sorbents has been done by sonication of the used sorbents for 15 min with 5 mL methanol as desorbent on ultrasonic bath. The recovery data of sorption studies are tabulated in Table 8.

4. Conclusion

From this work, it is evident that peels of lemon (*Citrus limonum*), mango (*Mangifera indica*), water melon (*Citrullus lanatus*), and melon (Cucumis melo) can be effectively

employed for Cr (VI) removal from wastewater streams of industries, like tanneries and textile industry. Their adsorption capacity can be effectively enhanced by base treatment. Among these samples, base-treated melon peels have more chemisorption capacity and water melon samples shown more physio-sorption capacity as compared to others, which is evident from isothermal investigations. Kinetic studies favor pseudo-second-order model that is the indication of the speedy sorption of Cr (VI) ions from solution onto the sorbing materials on initial stages, followed by diffusion to inner layers of sorbents. It is revealed by thermodynamic studies that the removal process of the Cr (VI) ions by the selected sorbents is spontaneous as well as exothermic in nature. The selected peels showed a decrease in their scavenging power in the presence of $NaSO_4$ and $NaCl$, but recovery of Cr (VI) ions is easy by washing with methanol. Therefore, it is recommended that the suggested home-grown biowaste materials can be employed for the treatment of waste water on industrial level before their discharge into freshwater bodies, which will be the start of Green era in wastewater treatment in Pakistan and other Asian countries to use cheap, indigenous, and user-friendly methodologies for wastewater treatment using minimum chemicals in user friendly way, to resolve local issues with their own resources.

Data Availability

All data related to this work are presented in the Results section along with references.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publications of this paper.

Acknowledgments

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