

Research Article

Adsorption of Chromium(VI) from Aqueous Solutions by Coffee Polyphenol-Formaldehyde/Acetaldehyde Resins

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Removal of chromium(VI) from wastewater is essential as it is toxic. Thus, removal of chromium(VI) was performed using coffee polyphenol-formaldehyde/acetaldehyde resins as adsorbents. Adsorbent resins were prepared by condensation of decaffeinated coffee powder with formaldehyde/acetaldehyde and used for the removal of Cr(VI) ions from aqueous solutions. A simple and sensitive solid phase extraction procedure was applied for the determination of chromium at trace levels by spectroscopic method using 1,5-diphenylcarbazide reagent. The adsorption of Cr(VI) on the coffee polyphenol-formaldehyde/acetaldehyde resins was monitored by FTIR and EDX analysis. The metal adsorption parameters such as contact time, pH, Cr(VI) ion concentration, and adsorbent dose were investigated. For Cr(VI), the maximum adsorption capacity of coffee polyphenol-formaldehyde resins was 98% at pH 2. The experimental results showed that Cr(VI) bound strongly with coffee polyphenol-formaldehyde/acetaldehyde resins and utilization of resins could be improved greatly by reuse.

1. Introduction

Metal ions such as Cd, Cr, Co, Cu, Zn, Pd, Hg, Ni, Ag, and Sr and metalloids such as Se, As, and Sb are toxic beyond trace levels. Most of these trace elements are transition metals with variable oxidation states and coordination numbers. Strong exposure to Cr(VI) causes cancer in the digestive tract and lungs. It may also cause gastric pain, nausea, vomiting, severe diarrhea, and hemorrhage [1, 2].

Treatment of wastewater generated by industrial processes today is of prime concern. Various technologies have been developed over recent years and are available for the removal of toxic metal such as chromium from wastewater [3]. Chromium bearing wastewater originates from a variety of industrial processes such as electroplating, dichromate and basic chrome sulphate manufacturing, tannery, anodizing, cutting tools, and chrome mining. Many of these industrial processes usually produce a large volume of wastewater with a chromium concentration ranging from less than 1 ppm to 10 ppm.

The two common oxidation states of chromium observed in natural water are Cr(III) and Cr(VI). Cr(III) is not

a significant groundwater contaminant, whereas Cr(VI) is approximately 100 times more toxic than Cr(III) [4].

Conventional methods used for removing Cr(VI) ions from industrial wastewater include reduction followed by chemical precipitation, adsorption on activated carbon, solvent extraction, freeze separation, reverse osmosis, ion exchange, and electrolytic methods. These methods have found limited applications because they often involve high capital and operational costs. Adsorption is an effective and versatile method for removing chromium which solves the problem of sludge disposal and renders the system more economically viable, especially if low-cost adsorbents are used [5–9]. The major advantage of adsorption is its high selectivity and enrichment factor.

A wide range of commercial sorbents including chelating reagents and activated carbon are available for adsorption, but they are relatively expensive. In recent years, low-cost natural materials have been proposed as potential biosorbents. These include moss peat, algae, leaf mould, sea weeds, coconut husk, sago waste, peanut hull, hazelnut, bagasse, rice hull, sugar beet pulp, plant biomass, bituminous coal, and coffee powder [10–21].

High proportions of aromatic compounds present in coffee beans are phenolics, presumably derived from chlorogenic acid and melanoidins [20, 21]. Coffee melanoidins are formed on roasting coffee beans and they have the ability to chelate metal ions.

In the present study, adsorbent resins were prepared from condensation of coffee polyphenol and formaldehyde/acetaldehyde for Cr(VI) removal. The effect of various parameters on adsorption of Cr(VI) such as pH, contact time, Cr(VI) concentration, adsorbent dose, and desorption were investigated.

2. Materials and Methods

2.1. Materials. Roasted coffee beans were procured from a local source, crushed in a grinder, and sieved through 355 μm pore size filter. Sieved coffee powder was treated with chloroform to remove caffeine. The activated decaffeinated coffee polyphenol powder was further treated with formaldehyde/acetaldehyde solution in the presence of ammonia. Kinetic studies using batch experimental method were carried out for the removal of Cr(VI) from aqueous solutions. Acetaldehyde (35%), ammonia solution (25%), sulfuric acid (98%), and nitric acid (70%) were purchased from Merck, India. Formaldehyde (37% solution) was obtained from Qualigen, India. Stock solution of Cr(VI) (17.6 mg/mL) was prepared by dissolving accurately weighed potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, Loba Chemie Pvt. Ltd. Mumbai, India) in 100 mL deionized water. A solution (0.025%) of 1,5-diphenylcarbazide (DPC, Sigma-Aldrich, USA) was prepared by dissolving 25 mg of DPC in 5 mL of acetone (Merck) and 10 mL of 5 M H_2SO_4 . This mixture was diluted to 100 mL with deionised water and stored in an amber-glass bottle. Water was deionised and purified with a Milli-Q water purification system (Millipore, USA). Freshly prepared solutions were used for all experiments. All chemicals were used without purification.

2.2. Preparation of Coffee Polyphenol-Formaldehyde (CFA) Resin. The composition of reactants is illustrated in Table 1. In a 100 mL plastic container, 4 g of activated decaffeinated coffee powder and desired amount (5 to 25 mL) of 37% formaldehyde solution were added and stirred for 5 min to achieve uniform mixing. To this mixture, 10 mL ammonia (25%) solution was added and stirred for an additional 5 min. The resulting reaction mixture was kept for 15 days at room temperature. A precipitate was observed at the bottom of the plastic container. The reaction mixture was neutralized with 1 M hydrochloric acid solution and the precipitate formed was filtered using a filter paper. The precipitate was treated with 1.2 M hydrochloric acid solution to make it insoluble in both acidic and basic medium. The solution was filtered and the residue was treated with deionized water followed by drying at 80°C for 8 h so as to obtain insoluble coffee polyphenol-formaldehyde resins. Analysis of particle size was in the range of 20.85 to 28.29 μm . These resins were prepared in duplicate to check reproducibility and whether results obtained were within the same range.

TABLE 1: Composition of coffee polyphenol-formaldehyde (CFA) resins.

Resin code	Coffee powder (g)	Formaldehyde (mL)	Ammonia (mL)
CFA 01	4	5	10
CFA 02	4	10	10
CFA 03	4	15	10
CFA 04	4	20	10
CFA 05	4	25	10

TABLE 2: Composition of coffee polyphenol-acetaldehyde (CAA) resins.

Resin code	Coffee powder (g)	Acetaldehyde (mL)	Ammonia (mL)
CAA 01	4	5	10
CAA 02	4	10	10
CAA 03	4	15	10
CAA 04	4	20	10
CAA 05	4	25	10

2.3. Preparation of Coffee Polyphenol-Acetaldehyde (CAA) Resin. The composition of reactants is presented in Table 2. In a 100 mL plastic container, 4 g of activated decaffeinated coffee powder and desired amount (5 to 25 mL) of acetaldehyde solution (35%) were added and stirred for 5 min to achieve uniform mixing. To this mixture, 10 mL ammonia (25%) solution was added and stirred for an additional 5 min. The resulting reaction mixture was kept for 15 days at room temperature. A precipitate was observed at the bottom of the plastic container. The reaction mixture was neutralized with 1 M hydrochloric acid solution and the precipitate formed was filtered using ordinary filter paper. Precipitate obtained was treated with 1.2 M hydrochloric acid to make it insoluble in both acidic and basic medium. The solution was filtered and the residue was treated with deionized water followed by drying at 80°C for 8 h so as to obtain insoluble coffee polyphenol-acetaldehyde resins. Analysis of particle size was in the range of 16.71 to 26.23 μm . These resins were prepared in duplicate to check reproducibility and whether results obtained were within the same range.

2.4. Resin Characterization. IR spectra of resins were recorded on FTIR (PerkinElmer) spectrophotometer. The samples were prepared after drying the resins at 80°C for 4 h. Potassium bromide (spectrometry grade) was dried at 150°C for 4 h and pellets were prepared by mixing 1 mg of sample with 100 mg of potassium bromide. IR spectra were recorded from 4000 to 450 cm^{-1} (8 scans) on potassium bromide pellets. Scanning electron microscope (SEM) and EDX measurements were conducted using BRUKER AXS, X-flash detector 5010 at an acceleration voltage of 0–20 keV. Particle size distribution was determined using Accusizer 780 Optical Particle Sizer (PSS-Nicom, Particle Sizing System, Santa Barbara, CA, USA).

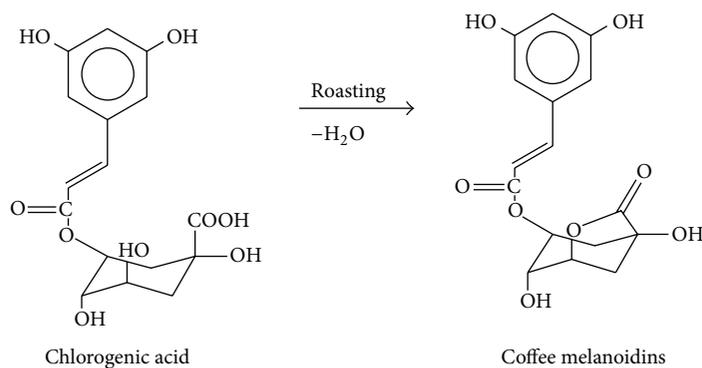


FIGURE 1: Chlorogenic acid and its roasted form.

2.5. *Adsorption of Cr(VI)*. Batch method was used to investigate the adsorption study of Cr(VI) onto CFA and CAA resins. To study the effect of pH on Cr(VI) sorption, 100 mg of resin was immersed into 10 mL (17.6 ppm) Cr(VI) stock solution at different pH. The mixture was stirred at room temperature for 24 h. The concentration of Cr(VI) ions in the effluent was determined spectrophotometrically by the development of a pink color with a complexing agent 1,5-diphenyl carbazide in acidic solution. Absorbance of the pink-colored solution was measured at λ 540 nm after 20 min against blank. Based on the optimum conditions, Beer's law holds well within the concentration range 0.08–0.51 mg/mL and the regression equation is $Y = 4.332X$ with a correlation coefficient of 0.9968.

3. Results and Discussion

3.1. *Coffee Polyphenol-Formaldehyde/Acetaldehyde Resin*. Aromatic compounds found in coffee beans are mainly phenolic compounds. Robusta coffee has slight higher phenolic content than Arabica [20, 21]. Decaffeinated coffee beans were crushed in a grinder and sieved through 355 μ m pore size filter. Sieved coffee powder was further treated with chloroform to remove alkaloids such as caffeine and trigonelline. The residue contains mostly chlorogenic acid and coffee melanoidins, useful from the resin's point of view [22, 23]. The structure of coffee melanoidins is presented in Figure 1. Adsorbents were prepared by condensation of decaffeinated coffee powder with formaldehyde/acetaldehyde in the presence of ammonia. Batch experiments were carried out to study the kinetics of removal of Cr(VI) from aqueous solutions.

Comparison plot of adsorption of chromium with blank coffee powder, coffee-polyphenol-formaldehyde, and coffee-polyphenol-acetaldehyde resins is shown in Figure 2 and it showed that the adsorption of blank coffee powder was lower than coffee-formaldehyde resins. Our objective was to develop new resins with coffee powder for toxic metal removal which should have better thermal and mechanical performance. So that, the same resins can be used repeatedly thus increasing turn over number which would be economically beneficial. Blank coffee powder does not have enough thermal or mechanical performance, because basically it contains organic compounds, which will not serve our purpose.

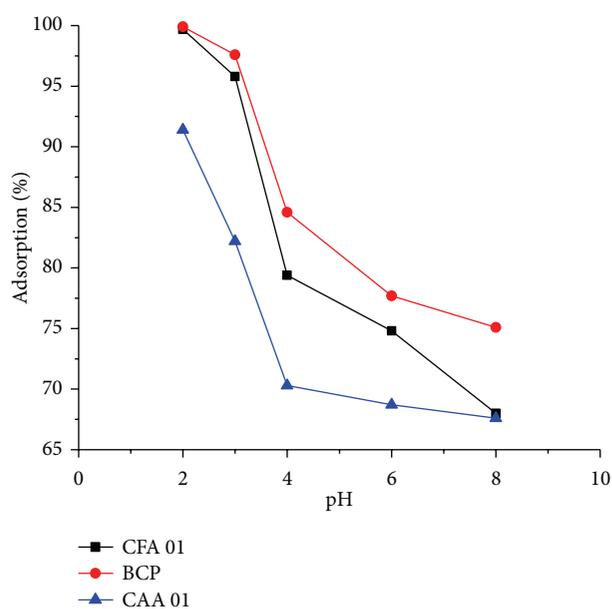


FIGURE 2: Comparison of coffee polyphenol based resins on chromium adsorption. CFA: coffee polyphenol-formaldehyde resins; CAA: coffee polyphenol-acetaldehyde resins; BCP: blank coffee powder.

In this case, formaldehyde acts as a cross-linker and forms coffee polyphenol-formaldehyde/acetaldehyde resins. Coffee contains polyphenols which are linked together by forming $-\text{CH}_2-$ bridges. The resins prepared by condensation polymerization of coffee polyphenols with formaldehyde/acetaldehyde are thus insoluble in acidic as well as basic media and increasing reusability and simultaneously turn over number.

Mainly two cross-linkers such as formaldehyde and acetaldehyde were studied to see the effect on chromium metal adsorption. It was observed that formaldehyde (pK_a , 13.3) showed higher chromium adsorption than acetaldehyde (13.57) due to more acidic nature and steric hindrance.

3.2. *Fourier Transform Infrared Analysis*. FTIR spectroscopy was used to identify the functional groups present in roasted coffee bean powder. Roasted coffee bean powder has a

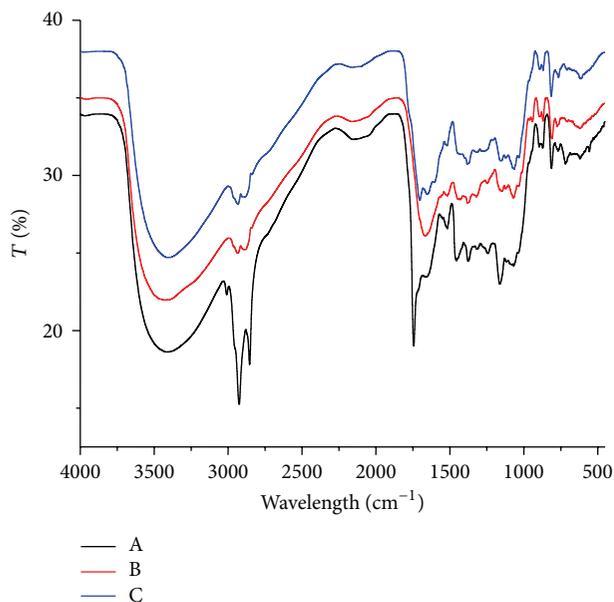


FIGURE 3: FTIR spectra of decaffeinated coffee powder (A), coffee polyphenol-formaldehyde resins (virgin) (B), and coffee polyphenol-formaldehyde resins with Cr(VI) (C).

variety of functional groups such as hydroxyl, carboxyl, carbonyl, amino and imino, which are important sites for metal sorption. The FTIR spectra of blank decaffeinated coffee powder (A), coffee polyphenol-formaldehyde resins (B), and Cr(VI) adsorbed coffee polyphenol-formaldehyde resins powder (C), respectively, are depicted in Figure 3. The absorbance bands observed at 3423 and 2934 are assigned to -OH and -CH_2 stretching, respectively. The sharp peak observed at 1744 cm^{-1} for decaffeinated coffee is due to the C=O stretching of carboxyl acid, ketone, or its ester. The small peak observed at 1080 cm^{-1} is due to the N=C stretching of caffeine. All the absorptions observed at 3423, 2934, 2884, 1744, and 1665 cm^{-1} are shifted to higher wavelength with adsorption of Cr(VI) ion. From these results, it is presumed that the Cr(VI) metal ion is incorporated with CFA resins through interaction with active functional groups such as -OH and -CO- .

3.3. Effect of pH. The pH of aqueous solution is a significant parameter for the removal of metal ions by adsorption [24]. Adsorption of Cr(VI) was studied in the pH range of 1–8 and the effect of pH on Cr(VI) removal using coffee-polyphenol-formaldehyde and coffee-polyphenol-acetaldehyde resins is shown in Figures 4 and 5, respectively.

The experimental results reveal that Cr(VI) removal efficiency increases with the decrease in pH and reached up to 99.7% at pH 2. Cr(VI) exists in aqueous phase in different anionic forms such as chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), or hydrogen chromate (HCrO_4^-) as depicted in Figure 6. The dominant form of Cr(VI) at lower pH is HCrO_4^- [25]. Shifts of HCrO_4^- to other forms CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ increase with the pH. From these results, it

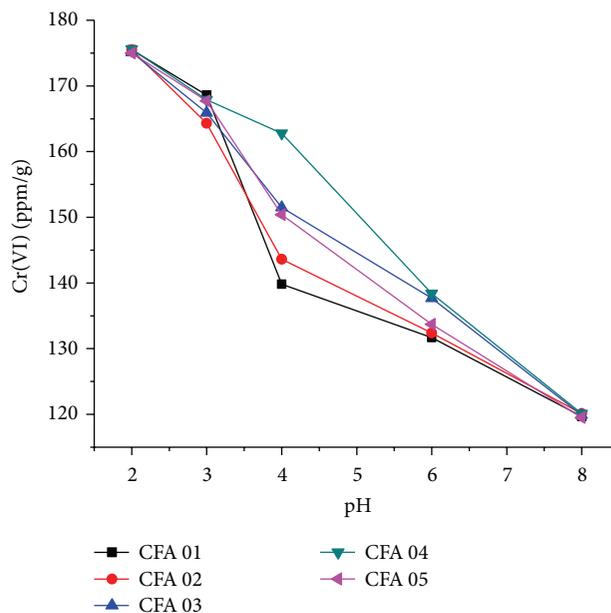


FIGURE 4: Effect of pH on Cr(VI) adsorption by CFA resins.

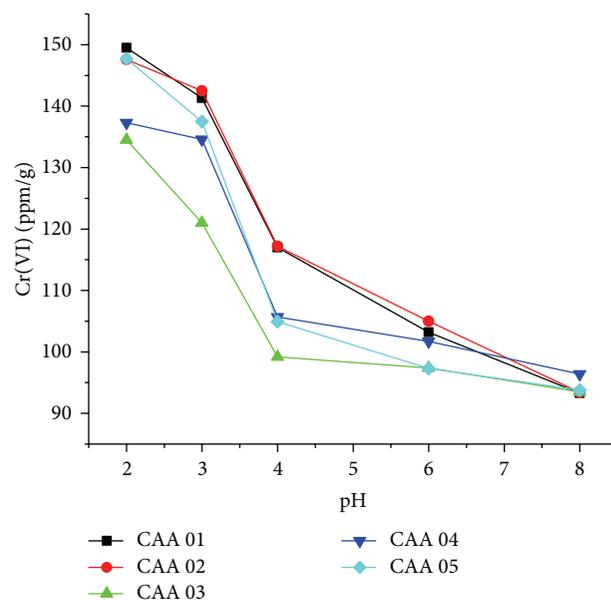


FIGURE 5: Effect of pH on Cr(VI) adsorption by CAA resins.

can be concluded that the active form of Cr(VI) can be adsorbed onto HCrO_4^- . The adsorption of Cr(VI) is more effective on coffee polyphenol-formaldehyde/acetaldehyde adsorbents. Some of the functional groups such as phenolic -OH bind electrostatically with negatively charged metal complexes. The decrease in the adsorption with increase in pH may be due to the decrease in electrostatic force of attraction between sorbent and sorbate ions. At lower pH, the percentage of Cr(VI) removal is high as the surface of adsorption becomes protonated; thus, the electrostatic force of attraction becomes high, resulting in an increase in the

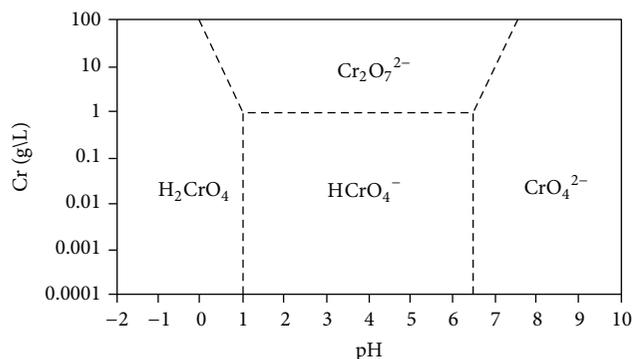


FIGURE 6: Speciation of Cr(VI).

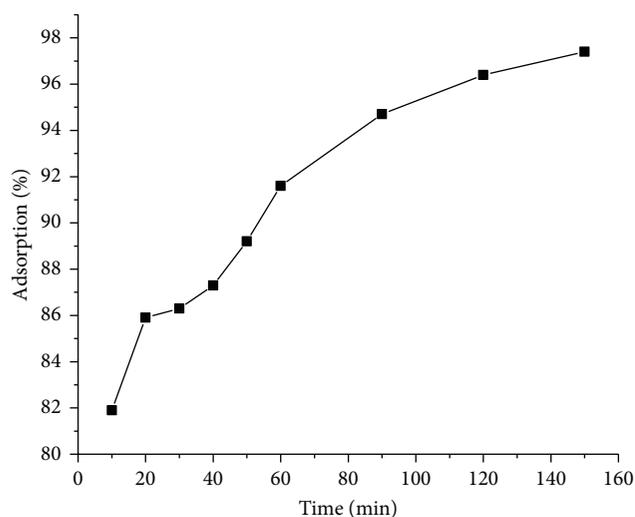


FIGURE 7: Effect of contact time on Cr(VI) adsorption.

attraction of anionic species of Cr(VI) towards adsorbent coffee resins. The decrease in adsorption above pH 4 may be due to saturation of the adsorption sites by anionic species like CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ which retards the adsorption of such ions further towards the adsorbent surface. In other words, as the pH increased above the zeta potential of the adsorbent there is a reduction in the electrostatic attraction between the Cr(VI) species and the adsorbent surface.

3.4. Effect of Contact Time. Time of contact has a significant influence on the adsorption of Cr(VI). The adsorption experiments were carried out with respect to contact time ranging from 10 to 150 min and the results are presented in Figure 7. The results indicated that metal adsorption increases with contact time. For the first 10 min, the percentage removal of Cr(VI) from aqueous solution increases rapidly and reaches a value of 81%; later on adsorption rate becomes slower and reaches up to 97% at 150 min. Further increase in contact time has a negligible effect on the percentage removal of Cr(VI). The fast initial uptake may be due to the accumulation of metal ions on the surface of adsorbent which is a rapid step.

The mechanism of solute transfer to the solid includes diffusion through the fluid film around the adsorbent particle

TABLE 3: Particle size analysis of coffee resins.

Sr. no.	Resin code					
	CFA	01	02	03	04	05
1	Particle size (μm)	—	28.89	18.79	28.43	20.85
	CAA	01	02	03	04	05
2	Particle size (μm)	16.71	26.23	20.64	22.70	20.77

and pores to the internal adsorption sites. Initially, the concentration gradient between the film and the solid surface is high, and hence the transfer of solute onto the solid surface is faster. Thus, it takes a smaller amount of time to attain 81% percent removal of Cr(VI). As the contact time increases, intraparticle diffusion becomes predominant. Hence, after 81% adsorption, solute takes more time in the transfer of Cr(VI) from solid surface to internal adsorption sites through the pores. Therefore, the optimum time for adsorption of Cr(VI) on coffee polyphenol-formaldehyde/acetaldehyde resins is 150 min for all batch studies.

3.5. SEM and EDX Analysis. The morphological analysis of coffee resins was performed by SEM as shown in Figure 8. Many small pores and particles $>5 \mu\text{m}$ diameter are observed on the surface of coffee polyphenol-formaldehyde/acetaldehyde resins. EDX spectrum (Figure 9) also showed a peak at 5.4 keV, which confirmed that Cr(VI) was adsorbed on coffee polyphenol-formaldehyde/acetaldehyde resins. It supports that the reaction of metal ion and phenolic $-\text{OH}$ group on coffee polyphenol-formaldehyde/acetaldehyde resins surface may be partly ion exchange or complexation. The results of analysis of particle size and particle size distribution are reported in Table 3. A plot of particle size distribution of coffee polyphenol-formaldehyde/acetaldehyde resins (CAA 05) is depicted in Figure 10. CFA resins showed higher particle sizes than CAA resins.

3.6. Effect of Chromium(VI) Concentration. Adsorption of Cr(VI) is significantly influenced by the concentration of Cr(VI) in aqueous solutions. The adsorption of Cr(VI) was examined with respect to the amount of Cr(VI) in solution. The Cr(VI) concentration varied from 5 to 20 ppm. The effect of initial concentration on percentage removal of Cr(VI) is depicted in Figure 11. The percentage removal of Cr(VI) decreases with the increase in initial Cr(VI) concentration. It may be due to an increase in the number of Cr(VI) ions for a fixed amount of adsorbent. The rate of percent Cr(VI) removal is higher at the beginning due to larger surface area of coffee resins being available for the adsorption. Once saturation point is reached the capacity of the adsorbent gets exhausted and uptake rate is controlled by the sorbate, transported from the exterior to the interior sites of the adsorbent particles. The results indicated that the initial Cr(VI) ion concentration determines the equilibrium concentration and also determines the rate of uptake of Cr(VI) ion and its kinetic character.

3.7. Effect of Adsorbent Dose. The various doses consisting of the adsorbents (100 mg to 300 mg) were mixed with metal

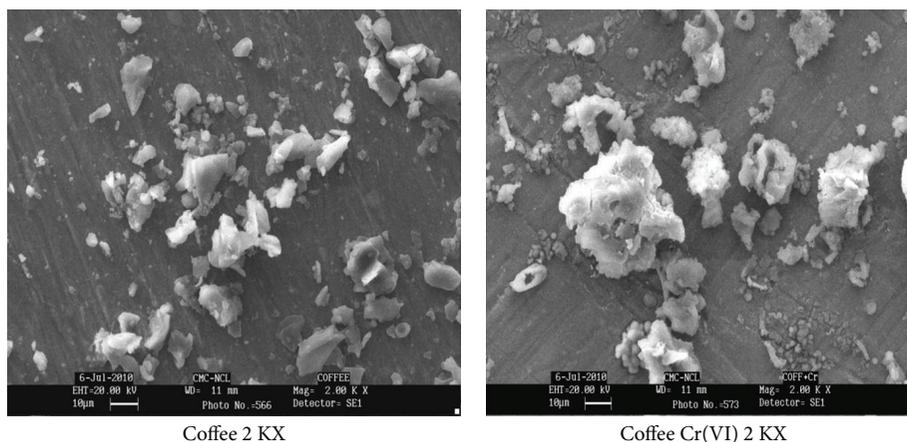


FIGURE 8: SEM photographs of coffee resins.

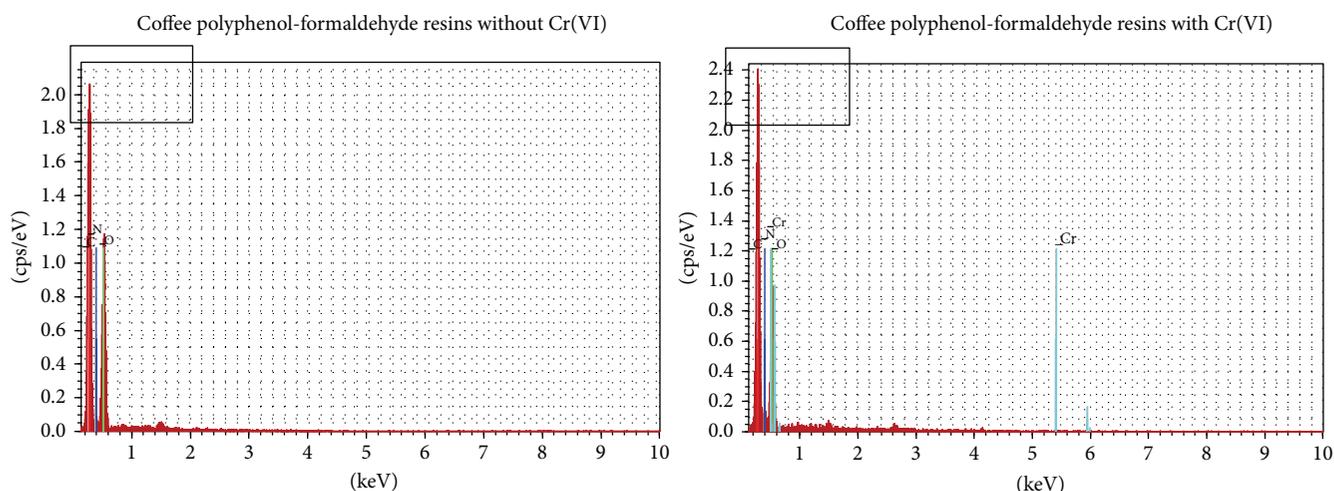


FIGURE 9: EDX spectra of coffee resins.

ion solutions and kept at room temperature for 24 h. The adsorption capacities for different doses were determined by keeping all other factors constant, for example, pH and temperature. The effect of adsorbent dose on the adsorption of Cr(VI) is presented in Figure 12. It is inferred that the percent removal of Cr(VI) increases with the increase in the weight of adsorbent dose (coffee resins). This may be due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent. If the adsorbent amount is increased by keeping the Cr(VI) concentration constant, then the amount of Cr(VI) adsorbed per unit mass decreased due to availability of lower number of Cr(VI) ions per unit mass of adsorbent. For 35.2 ppm of Cr(VI) concentration at pH 2, optimum values of percentage adsorption and adsorbent concentration are 99% and 200 mg, respectively.

3.8. Desorption Study. Desorption studies help to elucidate the nature of adsorption and recycling of the adsorbent. Adsorption of any solute on adsorbent takes place by physical bonding, ion-exchange, or a combination of both. If the adsorbed Cr(VI) is desorbed by water at neutral pH, then

the bonding of Cr(VI) with the adsorbent is physical. If hydrochloric acid or alkaline solution desorbed the Cr(VI), then the adsorption takes place by ion exchange. If organic acids, like acetic acid, desorbed the Cr(VI), then the Cr(VI) is held by chemisorption [26, 27]. Various eluents such as hydrochloric acid, nitric acid, and acetic acid are used. The effect of various eluents used for desorption studies indicates that hydrochloric acid is a better eluent for desorption, because results showed that the removal of adsorbed chromium ions was more than 75%. The reversibility of adsorbed Cr(VI) in mineral acid or base is in agreement with the pH dependent results obtained [28, 29].

The reusability of the resin is important to reduce the process cost. Desorption was performed by using 1M hydrochloric acid. The metal desorbed resin was reused for three times and it shows good results. Figure 13 represents the adsorption-desorption cycle of CFA 01 resin. There was no significant change in adsorption capacity after three cycles. Adsorption capacity of resin after the third cycle was reduced by 8.68% compared to the first cycle. Also, it was observed that desorption capacities were 75, 72, and 62% for the first,

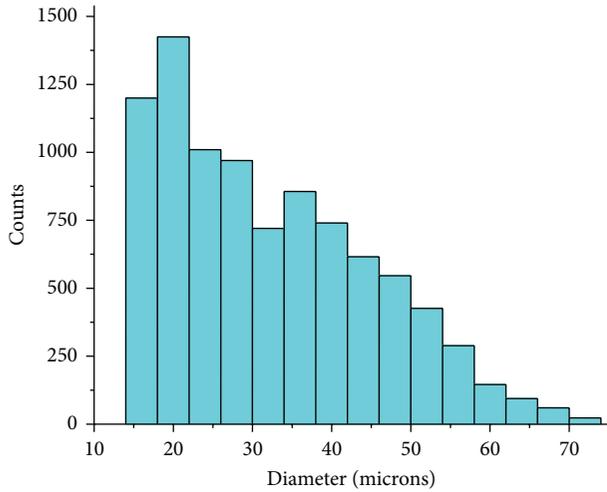


FIGURE 10: Particle size distribution of coffee resins.

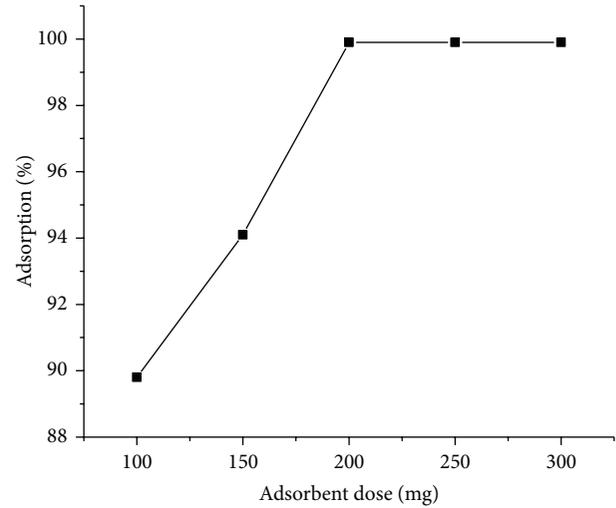


FIGURE 12: Effect of adsorbent dose on Cr(VI) adsorption.

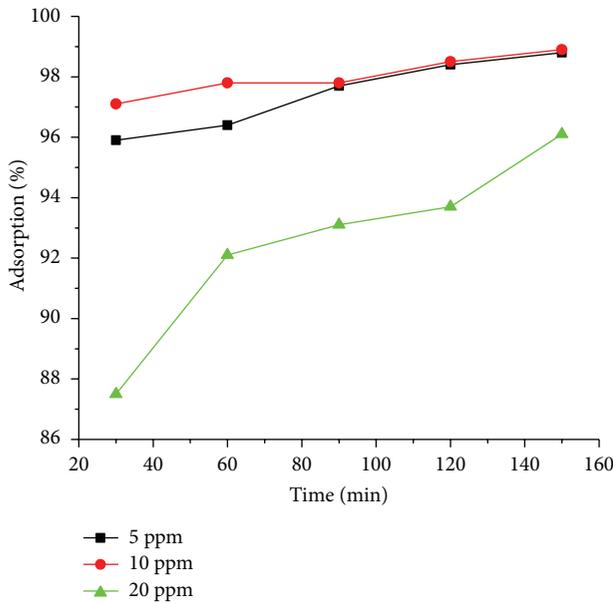


FIGURE 11: Effect of Cr(VI) concentration on adsorption.

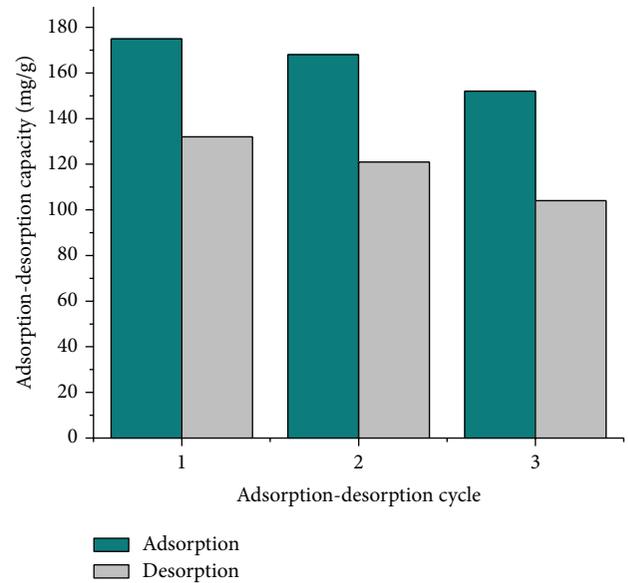


FIGURE 13: Adsorption-desorption cycle of CFA 01 resin.

second, and third cycle, respectively. These results show that coffee resins are effective and efficient adsorbent for Cr(VI) recovery.

3.9. Adsorption Isotherm. Adsorption isotherms of Cr(VI) were investigated with respect to biomaterials using an electrolyte solution at the optimum pH 2. The adsorption data were fitted by least square method to linearly transformed Freundlich and Langmuir adsorption isotherms.

The Freundlich adsorption isotherm was applied for the adsorption of Cr(VI) onto coffee polyphenol-formaldehyde resins. The linear Freundlich equation is mentioned below:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e, \quad (1)$$

where q_e is the amount of Cr(VI) adsorbed per unit mass of adsorbent (mg/g), C_e is the residual concentration of Cr(VI) in solution (mg/L), K_f is a constant which is a measure of adsorption capacity, and $1/n$ is a measure of adsorption intensity. The linear Freundlich adsorption isotherm is shown in Figure 14.

The Langmuir adsorption was applied to the present study to estimate the adsorption capacity of coffee polyphenol-formaldehyde resins. The linear form of the Langmuir adsorption isotherm is presented below:

$$\frac{C_e}{q_e} = \frac{1}{Q_0^b} + \frac{C_e}{Q_0}, \quad (2)$$

where C_e is the equilibrium concentration (mg/L) and q_e is the amount of Cr(VI) adsorbed per gram at equilibrium

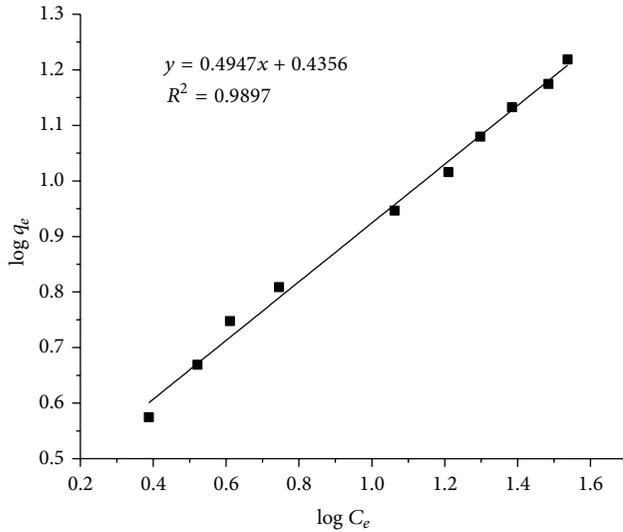


FIGURE 14: Freundlich isotherm for adsorption of Cr(VI).

TABLE 4

Q_0 mg/g (calculated)	Q_0 mg/g (found)	b (L/mg)	R^2
16.551	19.342	0.1007	0.9485

TABLE 5

K_f mg/g (calculated)	q_e mg/g (found)	n	R^2
0.3517	2.727	2.0214	0.9897

(mg/g). Q_0 (mg/L) and b (adsorbent per mg of adsorbate) are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively.

The results obtained from the adsorption experiments conducted at room temperature are fitted in Langmuir equation; linear plot was obtained for C_e/q_e versus C_e and is depicted in Figure 15. The high value of correlation coefficient ($R^2 = 0.948$) indicates a good agreement with the parameters and confirms the monolayer adsorption of Cr(VI) onto the adsorbent surface. The isotherm data is linear using the Freundlich and Langmuir equations. The high value of correlation coefficient ($R^2 = 0.989$) was found to be in good agreement with Freundlich equation.

These results indicated that adsorption of Cr(VI) followed both adsorption isotherm models. Freundlich isotherm model is fitted better than Langmuir, because the correlation between calculated and experimental (found) values as well as regression factors is in good agreement with Freundlich isotherm rather than Langmuir.

Langmuir constants were determined and are presented in Table 4.

Freundlich constants were determined and are depicted in Table 5.

To evaluate sorption dynamics, it requires consideration of two important physicochemical parameters such as kinetics and equilibrium of adsorption. Kinetics describe the solute uptake rate which governs the contact time.

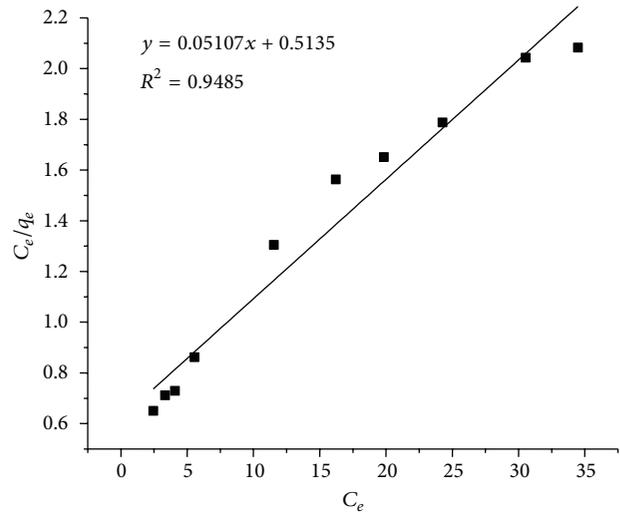


FIGURE 15: Langmuir isotherm for adsorption of Cr(VI).

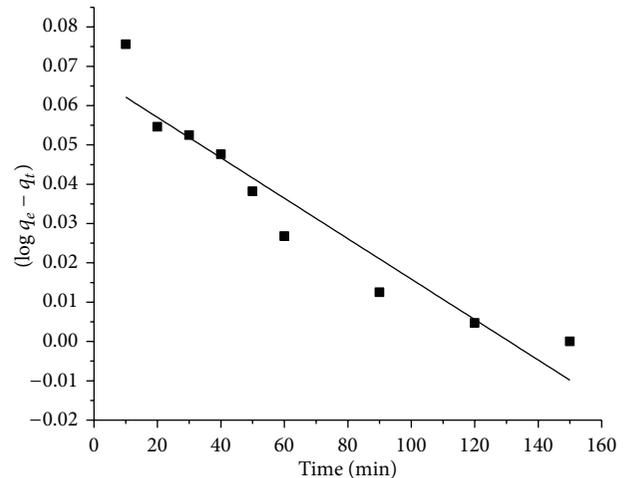


FIGURE 16: Pseudo-first order reaction.

The study of equilibrium is determining the distribution of solute between solid-liquid phases and determining the feasibility and capacity of the sorbent for adsorption. Several kinetic models, currently in use to explain the mechanism of adsorption progress, are most simple and widely used is pseudo-first order equation of Lagergren [30]:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}t}{2.303}, \quad (3)$$

where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t is mass of metal adsorbed at time t (mg/g), and K_{ad} is the first order reaction constant (L/min). The pseudo-first order considers that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. A straight line of $\log(q_e - q_t)$ versus t indicates the application of the first order kinetic model (Figure 16).

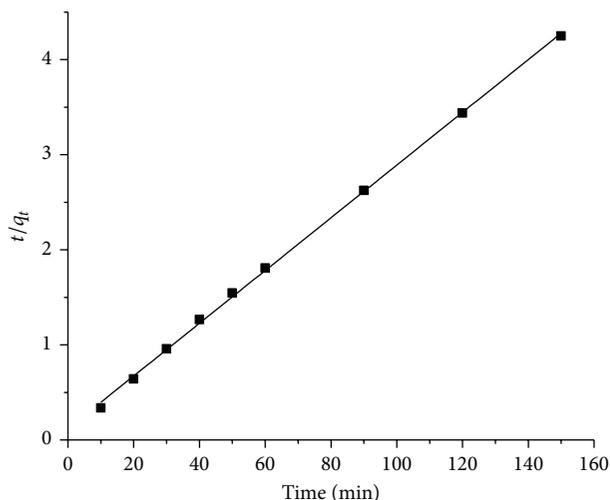


FIGURE 17: Pseudo-second order reaction.

TABLE 6: Comparison of adsorption of Cr(VI) with naturally occurring adsorbents.

Sr. no.	Biosorbent	Cr(VI) (mg/g)	Reference no.
1	Rice husk carbon	45.6	[31]
2	Iron(III) hydroxide	0.47	[32]
3	Waste tea	1.63	[33]
4	Irish sphagnum moss peat	119	[34]
5	Saw dust	10.1, 16.05, 4.44	[35–37]
6	Blast furnace slag	7.5	[38]
7	Activated red mud	1.6	[39]
8	Waste tyre	58.48	[40]
9	Olive cake	33.44	[41]
10	Distillery sludge	5.7	[42]
11	Coffee husk	44.95	[43]
12	CFA and CAA resins	175.44, 143.32	This study

On the other hand, equilibrium capacity may be expressed by pseudo-second order equation as follows:

$$\frac{t}{q_t} = \frac{1}{K_{2ad}q_e^2} + \frac{t}{q_e}, \quad (4)$$

where K_{2ad} is the second order reaction rate equilibrium constant (g/mg·min). A plot of t/q_t versus t gives a linear relationship for the applicability of the second order kinetic model (Figure 17).

The adsorption capacity of coffee polyphenol resins compared to other materials is reported in the literature [31–43] and is given in Table 6. The sorption capacity of CFA and CAA resins are 175.44 and 143.32 mg/g, respectively, which are higher than adsorbents reported in the literature such as industrial as well as low-cost natural materials. And the second advantage is that resins can be reused number of times by adsorption-desorption method due to better thermal and mechanical performance than without cross-linked natural materials, ultimately reducing the cost.

Most of the low-cost adsorbents have the limitations such as low adsorption capacity and also generate more solid waste causing disposal problems. Hence, there is a need to explore low-cost adsorbents with high adsorption capacity. In our study, we have prepared particulate systems where average particle size ranges are 20.85 to 28.89 μm for CFA resins and 16.71 to 26.23 μm for CAA resins.

4. Conclusion

The use of bioadsorbent prepared from coffee powder, capable of adsorption of Cr(VI) from aqueous stream, is cost effective and efficient. The maximum adsorption of Cr(VI) took place at pH 2. The active form of Cr(VI) adsorbed onto coffee polyphenol-formaldehyde/acetaldehyde resins at lower pH is found to be HCrO_4^- . The percentage of the removal of Cr(VI) decreases with the increase in pH. The adsorption process of Cr(VI) is described by Freundlich and Langmuir isotherm models. However, Freundlich isotherm model shows a better agreement with the equilibrium data. The kinetic studies indicate that Cr(VI) adsorption on coffee polyphenol-formaldehyde/acetaldehyde resins is very fast (within the first 150 minutes). Percentage removal of Cr(VI) increases and adsorption capacity decreases with the increase in adsorbent amount, because of the availability of more adsorption sites. These results demonstrate the great potential of coffee polyphenol-formaldehyde/acetaldehyde resins which provide a convenient and low-cost adsorbent for heavy metal removal. Heavy metal ion Cr(VI) removal technique using such biomaterials would be an effective method for economic treatment of wastewater.

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