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Removal of hexavalent chromium from aqueous solution: a comparative study of cone biomass of "*Picea smithiana*" and activated charcoal

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ABSTRACT

The present work investigates comparative adsorption efficiency of powdered cone biomass of *Picea smithiana* (PCBP) and activated charcoal (AC) for removal of hexavalent chromium (Cr) (Cr(VI)) from aqueous solution. The study indicates that PCBP has 76% removal efficiency for Cr as compared to AC. Particle size and SEM-EDX analyses were done to determine average particle size, surface morphology and elemental composition of PCBP. BET and FTIR analysis were carried out to elucidate the adsorption mechanism of Cr(VI) on PCBP. Ashing has been proposed as a method for managing waste of loaded PCBP generated in adsorption. Ashing studies showed the ash content of PCBP to contribute only 13% of the ash generated from loaded biomass. Further, a comparative study has been made indicating the adsorption efficiency of PCBP with previously reported bio-waste materials. The results of this study show that PCBP has high adsorption efficiency as compared to other bio-waste materials.

Keywords: Hexavalent chromium; Cone biomass of *Picea smithiana*; Adsorption; Langmuir isotherm; Activated charcoal

1. Introduction

Chromium (Cr) is a heavy metal with widespread use in many industries like steel production, chrome plating, anodizing of aluminium, dye and paint production, textile dyeing, tanning of leather, wood preservation and water-cooling [1–7] and is discharged in wastewater from these industries. Owing to the hazardous nature of Cr containing effluents, removal of Cr from wastewater is mandatory as per environmental regulating agencies. As per US EPA, maximum limit for Cr(VI) discharge into surface water is 0.05 mg/L [8], while according to Indian standards, the permissible limit is 0.1 mg/L [9,10]. Various methods like ion exchange, chemical precipitation, membrane process, and adsorption and are used for removal of Cr from wastewater. Adsorption using charcoal as adsorbent is the most preferred and widely used technique [11].

Currently, many low-cost, biodegradable and highly efficient materials are under investigation for Cr removal which can be used as alternatives for non-biodegradable and high cost charcoal. Among the several materials under exploration, bio-waste

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materials as adsorbents have the advantage of easy availability, low-cost, high efficiency and generation of minimum amount of sludge. There is a possibility of biomass regeneration and metal recovery as well [12]. Although a number of bio-waste materials have been studied for removal of different heavy metals, however, only few of them can be commercialized as their adsorption efficiency remains much less as compared to charcoal. In the present work, powdered cone biomass of *Picea smithiana* (PCBP) has been investigated as bio-adsorbent for removal of Cr from aqueous solution and the efficiency has been compared with commercially available charcoal. Further, an attempt has been made to elucidate the mechanism of Cr adsorption by PCBP. PCBP is an ornamental, large, evergreen tree grown in western Himalayas. The plant bears long cylindrical cones (male and female) in very large amount which fall on surface after maturing. Locally, these cones are not of much use and are considered source of foul smell on degradation. To combat the problem, these are in general collected and burnt. However, these have been supposed to be rich in lignocelluloses which had been reported to have good adsorption efficiency for heavy metals [13,14]. The current work is an attempt for exploring Cr adsorption efficiency of PCBP. The study may be useful for the Cr discharging industries located in areas with high production of PCBP, as these may find a cost-effective substitute for charcoal.

2. Materials and methods

Cones of PCBP were collected from Baramulla district, Jammu and Kashmir, India, during the month of August 2012. The collected material was first washed with distilled water then air-dried for 48 h followed by oven drying at 60˚C for 24 h. The material was grinded and sieved through mesh of size 300 μm. The sieved material was stored in airtight polythene bags for further use. All chemicals used were of analytical grade from Loba Chemie Pvt. Ltd., Mumbai.

Activated charcoal (AC) was purchased from Fisher Scientific, Mumbai. The particle size of AC used was below 100 μm. Stock solution of 1,000 mg Cr/L was prepared by dissolving $K_2Cr_2O_7$ in double distilled water. Further dilutions were made from this stock solution by adding distilled water. Sulphuric acid (H_2SO_4) and sodium hydroxide were used to maintain the pH of Cr solution. Cr was analysed spectrophotometrically by 3500-Cr B Colorimetric Method [15] using UV-visible spectrophotometer (SHIMAZDU, UV-2450). All the experiments were performed in triplicate.

2.1. Characterization of the adsorbent material

2.1.1. Particle size analysis

Particle size of the selected material was determined by Mastersizer 2000 of Malvern Instruments Ltd. Malvern UK using Hydro 2000MU (A) accessory in the size range of 0.100–1,000 μm using water as dispersant for analysis.

2.1.2. Scanning electron microscopy and energy dispersive X-ray (SEM-EDX) analysis

Surface morphology and elemental composition of raw PCBP (PCPB before adsorption) and PCBP after Cr adsorption (500 mg/L aqueous solution of Cr(VI) at pH 2) was done using SEM (ZEISS EVO 40 EP) and EDX analysis (BRUKER LN_2 Free X-Flash 4010SDD Detector), respectively.

2.1.3. FTIR analysis

FTIR spectra of the raw PCBP, PCBP after Cr adsorption (500 mg/L aqueous solution of Cr(VI) at pH 2) and acid (pH 2)-treated PCBP were recorded on BRUKER TENSOR 27 Fourier transformation infrared spectrometer using KBr pellet method.

2.1.4. BET adsorption experiment

Nitrogen adsorption isotherms were obtained on a multipoint BET instrument (ASAP 2010) using approximately 0.5–0.9 g of sample for each measurement. Prior to the N_2 adsorption, each sample was vacuum degassed at 77 K for 3 h. The specific surface area was calculated by BET method using ASAP 2010 V5.02 software. The equilibrium interval for the adsorption and desorption experiment was kept at 5 s.

2.1.5. Element analysis

Elemental Analysis (CHNS) of PCBP was performed on a Flash 2000 Thermo elemental Analyzer. Further, the oxygen content of the adsorbent was determined by difference calculation Eq. (1).

$$\begin{aligned}\text{Oxygen}\,(\%) = {} & 100 - \text{Ash content}\,(\%) - \text{Carbon}\,(\%) \\ & - \text{Hydrogen}\,(\%) - \text{Nitrogen}\,(\%) \\ & - \text{Sulphur}\,(\%)\end{aligned} \tag{1}$$

2.2. Batch adsorption studies

2.2.1. Effect of contact time

The effect of contact time on Cr(VI) adsorption was studied by adding 2.0 g/L of PCBP and AC to 200 mL of 200 mg/L solution of Cr(VI) maintained at pH 4.5 and shaking different sets at 200 rpm for varying contact time (1–24 h). The solutions were filtered immediately after the due time interval using Whatman filter paper No. 1, and the filtrate was analysed for the concentration of Cr(VI).

2.2.2. Effect of pH

The effect of pH on adsorption of Cr(VI) was studied by adding 2.0 g of PCBP and AC separately to 200 mL of 200 mg/L Cr(VI) solution, maintained at pH 1, 2, 3, 3, 4, and 5 (adjusted using H_2SO_4). The flasks were shaken for 2 h in incubator shaker and then left for 22 h to attain equilibrium at 25 ± 1˚C. The solutions were filtered and the filtrate was analysed for concentration of Cr(VI).

2.2.3. Effect of adsorbent doses

The effect of adsorbent dose on Cr(VI) adsorption was studied by addition of 0.125–6 g/L adsorbent dose in 200 mL of 200 mg/L Cr(VI) solution taken. The flasks were shaken for 2 h at 200 rpm, 25 ± 1˚C and left for 22 h to achieve the equilibrium state. The solutions were then filtered, and the aqueous phase concentration of Cr(VI) was analysed.

2.2.4. Effect of initial metal ion concentration

The effect of initial metal ion concentration was studied by shaking 0.25 g/L of PCBP and AC separately with 200 mL of 100, 200, 300, 400, 500, and 600 mg/L Cr(VI) solution at pH 2 for 2 h. Then, all the flasks were left for 22 h at 25 ± 1˚C to attain equilibrium. The solutions were then filtered, and the aqueous phase concentration of Cr(VI) was analysed.

2.3. Data analysis

The adsorption capacities of both the materials (PCPB and AC) were calculated by fitting the data to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{S} \tag{2}$$

where q_e = metal ion uptake by adsorbent after equilibrium, mg/g; C_0 = initial concentration of metal ion in aqueous solution, mg/L; C_e = equilibrium concentration of metal ion after adsorption has occurred, mg/L; V = volume of aqueous solution treated, L; S = amount of adsorbent taken, g.

Further, percent removal ($R\%$) of Cr(VI) was determined by the equation given below:

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{3}$$

2.4. Adsorption isotherms

Langmuir isotherm equation (Eq. (4)) was fitted to the data obtained from the experiment carried out to study the effect of variation in initial Cr(VI) ion concentration:

$$\theta = \frac{(q_e)}{q_m} = \frac{(bC_e)}{(1 + bC_e)} \tag{4}$$

where θ = fractional coverage; b = k_a/k_d; k_a = adsorption constant; k_d = desorption constant; q_m = quantity of adsorbate required to form a single monolayer on unit mass of adsorbent, mg/g; q_e = amount of metal ions adsorbed on unit mass of the adsorbent at equilibrium, mg/g.

By rearranging the above equation, the linear equation for Langmuir isotherm can be written as follows:

$$\frac{(C_e)}{q_e} = \frac{1}{b\, q_m} + \frac{1}{q_m} \times C_e \tag{5}$$

where C_e is the equilibrium concentration of solute in bulk solution (mg/L) and b is the Langmuir constant related to the free sorption energy (L/mg). If this equation is obeyed by the adsorption equilibrium data, then plot of (C_e/q_e) should be a straight line. From slope and the intercept of the trend line, the values of q_m and b can be derived. Moreover, Langmuir equation also provides information on the process feasibility on the basis of dimensionless factor R_L. R_L can be derived using the following equation:

$$R_L = \frac{1}{(1 + bC_e)} \tag{6}$$

If value of R_L is between 0 and 1, then adsorption is favourable. R_L is greater than 1 indicates unfavourable adsorption, R_L equal to 1 indicates linear adsorption and if R_L equals to 0 is the indicator of irreversible adsorption.

2.5. Adsorption kinetics

The data obtained from the experiment carried out to study the effect of contact time were suitably fitted to various rate law equations, and the kinetics of the adsorption was established based on the best fit.

2.6. Thermodynamic studies

Thermodynamic study of Cr(VI) adsorption on PCBP was done by shaking 1 g of the adsorbent with 200 mL of 300 mg/L Cr(VI) solution at pH 5 and for 2 h at varying temperatures (288, 298, and 308 K), and then left for 22 h at same temperature to attain equilibrium. The Gibbs free energy of adsorption (ΔG) and the thermodynamic equilibrium constant (K_c) were obtained at different temperatures using the following equations:

$$K_c = q_e/C_e \tag{7}$$

$$\Delta G = -\mathrm{RT} \ln K_c \tag{8}$$

where

R = gas constant

T = temperature in Kelvin

Further, the changes in enthalpy and entropy were determined using the following equation:

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

A graph (ΔG vs. T) was plotted and its slope and intercept of the plots of were used to compute the value of ΔH and ΔS.

2.7. Ashing studies

The Cr-loaded PCBP sample was prepared by treating 10 g of PCPB with one litre of 5 g/L Cr(VI) solution maintained at pH 2. The ashing of the air-dried cone biomass and Cr-adsorbed cone biomass sample was carried out at 590°C [16].

3. Results and discussion

3.1. Characterization of the selected material

3.1.1. Particle size analysis

The results of the particle size analysis of PCBP (Fig. 1) revealed that major fraction of particles lie in the range of 20–400 μm which is 85.53%. The specific surface area of the PCBP material is 0.321 m^2/g, and the uniformity of the material is 1.01.

3.1.2. SEM-EDX analysis

The resultant electron micrographs and EDX spectra obtained from SEM-EDX analysis of the raw PCBP and PCBP after Cr adsorption are shown in Figs. 2–5, respectively. In case of raw PCBP, the electron micrographs showed that pore spaces are not much evident. However, PCBP after Cr adsorption showed quite visible pore spaces. This is because, under acidic

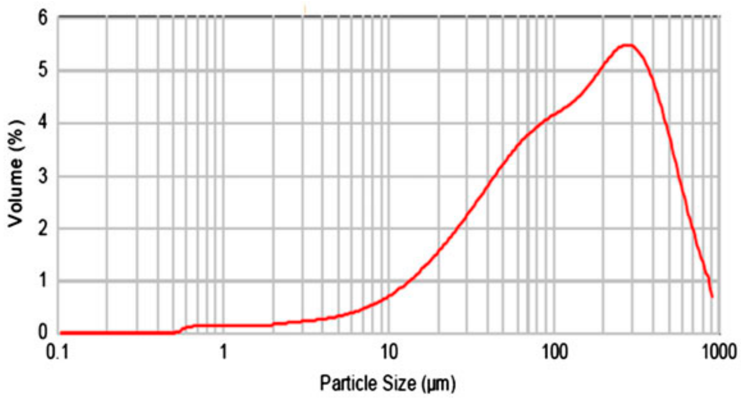

Fig. 1. Particle size distribution of PCBP.

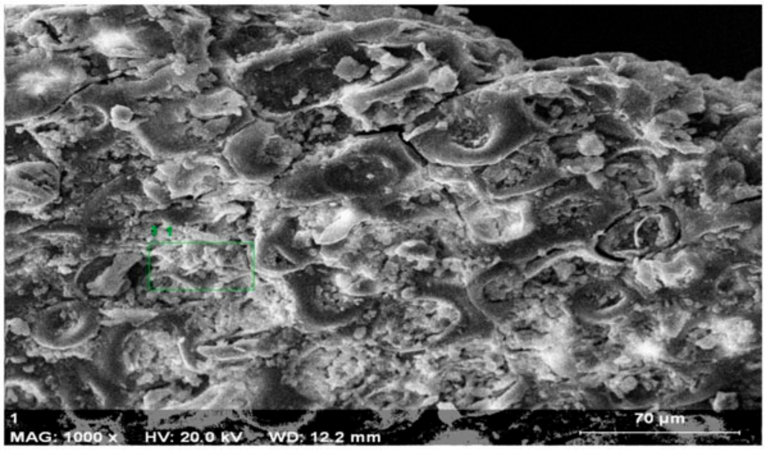

Fig. 2. Electron micrograph of raw PCBP.

conditions, the surface area of lignocellulosic materials increases due to the separation of lignin and cellulose [17] and consequently the pores get exposed to the environment.

As the PCBP is carbonaceous and lignocellulosic in nature, the EDX spectra of raw PCBP and PCBP after Cr adsorption show high percentage of carbon and oxygen, while the other elements such as magnesium, potassium, silicon, aluminium, and sulphur are present in minute concentrations. In EDX spectra of raw PCBP, Cr was completely absent, however, it was observed in EDX spectra of PCBP after adsorption. The appearance of sulphur in EDX spectra of PCBP after adsorption is attributed to addition of H_2SO_4, used for maintaining pH of the solution.

3.1.3. FTIR analysis

The FTIR spectra of raw PCBP, PCBP after Cr adsorption and PCBP acidified at pH 2 have been presented in Fig. 6. The FTIR spectra of PCBP revealed the presence of characteristic broad absorption bands at 3,351 cm^{-1} for hydrogen bonding, OH and NH_2 groups. The absorption band at 1,744 cm^{-1}

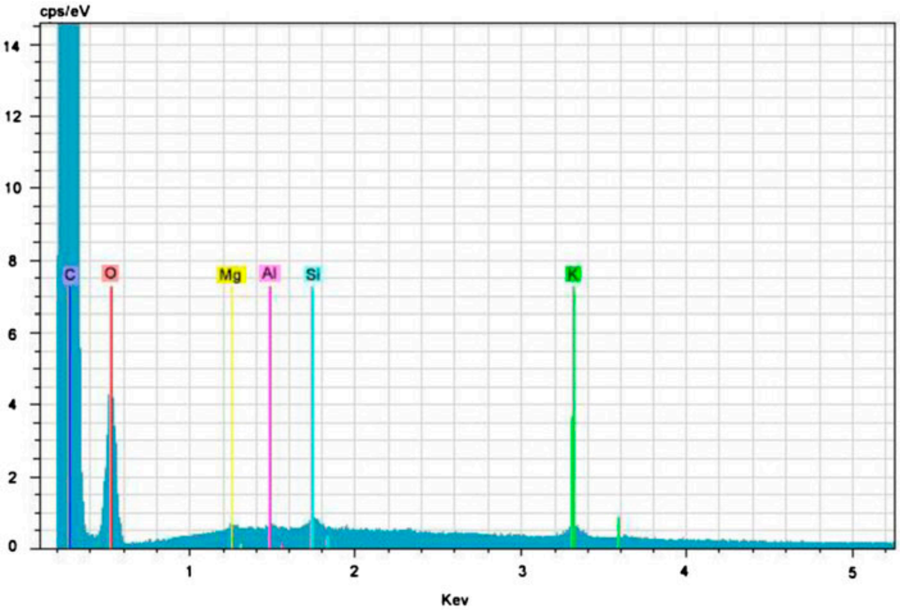

Fig. 3. EDX spectra of raw PCBP.

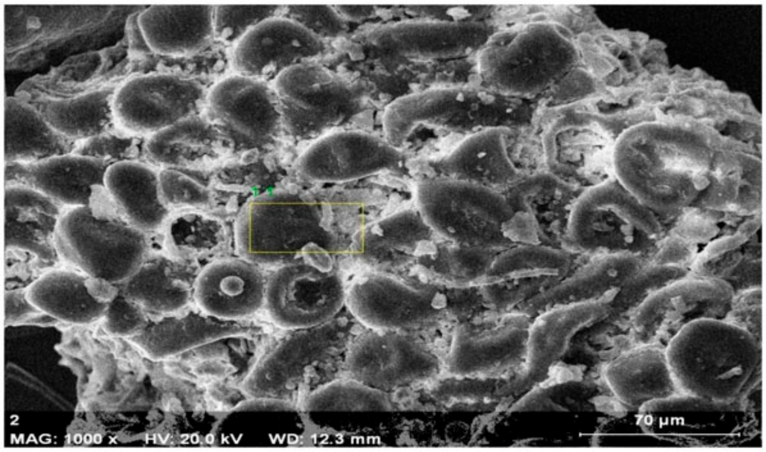

Fig. 4. Electron micrograph of PCBP after Cr adsorption (aqueous solution of Cr(VI) (500 mg/L) at pH 2).

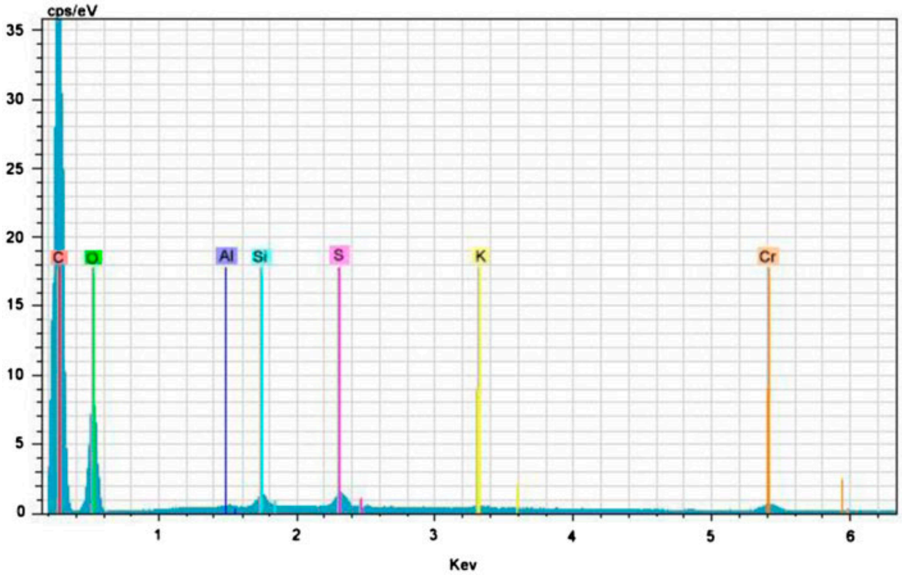

Fig. 5. EDX spectra of PCBP after Cr adsorption (aqueous solution of Cr(VI) (500 mg/L) at pH 2).

was attributed to the stretching vibration of free carbonyl from carboxylic groups. The relatively broad absorption bands around 1,663–1,607 cm^{-1} can be attributed to the stretching vibration of the carbonyl moieties present in various functional groups like amide, aldehyde and ketone. The absorption bands at 1,030, 1,164, and 1,269 cm^{-1} were attributed to guaiacyl moiety of lignin components in the biomass sample [18]. The bands at 1,469 and 1,513 cm^{-1} were attributed to methoxy deformation and vibration of aromatic skeleton, respectively. The absorption bands at 1,060 and 1,381 cm^{-1} were characteristic of carbohydrate units of cellulose and hemicellulose components of raw PCBP, respectively [19].

Further, FTIR spectrum of PCBP treated with aqueous solution of pH 2 showed substantial shift in the absorption band of hydroxyl group from 3,351 cm^{-1} in raw PCBP to 3,371 cm^{-1}. The shift in the absorption band of the hydroxyl group was attributed to the proton neutralization of the PCBP due to acid treatment. Further, the absorption band at 1,513 cm^{-1} was intensified, which could be attributed to increase in lignin content due to the dissolution of the partially hydrolysed hemicellulose and/or cellulose component of the PCBP under acidic conditions [20].

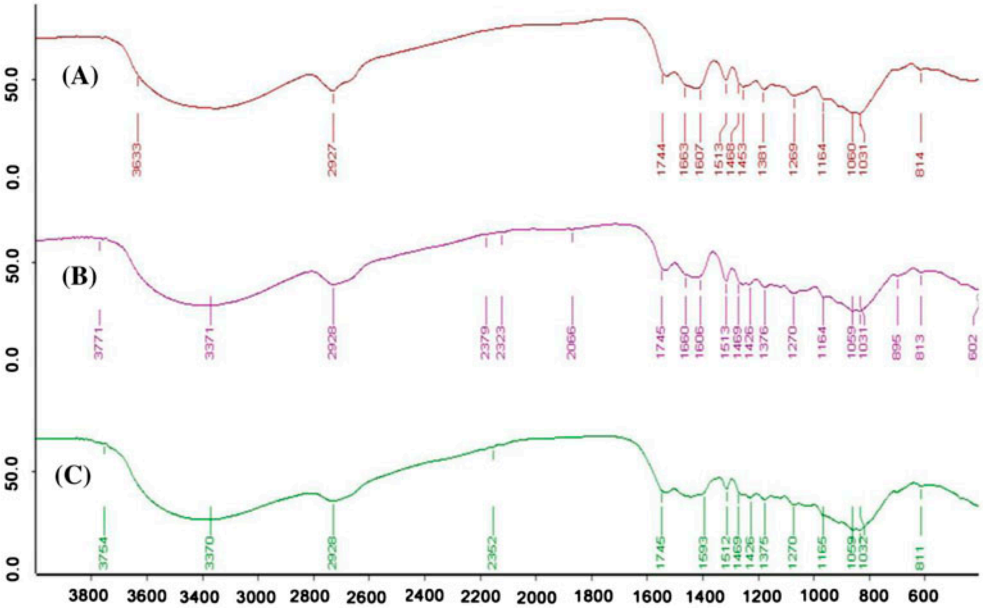

Fig. 6. FTIR spectra of (A) raw PCBP, (B) PCBP treated with aqueous solution at pH 2 using H_2SO_4 and (C) PCBP after Cr adsorption (aqueous solution of Cr(VI) (500 mg/L) at pH 2).

Upon adsorption of Cr under acidic conditions (pH 2), significant changes in the functional groups of the PCBP were observed. An absorption band in the range of 1,667–1,700 cm^{-1} was observed, which is a strong indication of the oxidation of hydroxyl groups. These observations are a strong evidence for oxidation of the lignin phenolic moieties to quinone moieties. Further, it has been observed that the absorption band at 1,513 cm^{-1} was of similar intensity as the raw PCBP, which suggests that the Cr ions in the solution coordinates and bind with hemicellulose units on the surface of the biomass. Thus, acidification leads to the swelling of the biomass with partial removal of crystalline cellulose and hemicellulose. In the presence of Cr, solubilised hemicellulose binds to lignin-reduced Cr(III) at the surface of the biomass. This leads to Cr being sandwiched between the lignin and hemicellulose. These results are significant, as compared to the two major mechanisms proposed for the Cr adsorption [21]. The possible mechanism is depicted in Fig. 7. Thus, comparative FTIR of the three materials reveals the binding mode of the material to be dependent upon the lignin and the hemicellulose content of the cone biomass.

3.1.4. BET adsorption experiment

The N_2 adsorption–desorption isotherms of PCBP are shown in Fig. 8. The surface area of the PCBP

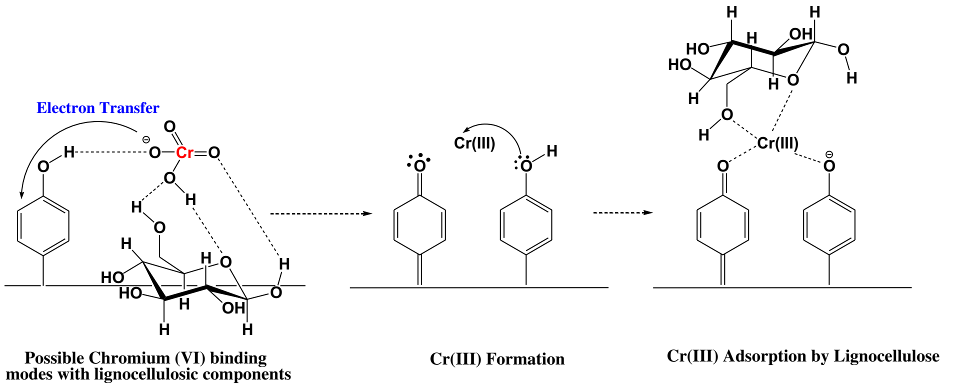

Fig. 7. Mechanism of Cr adsorption by PCBP.

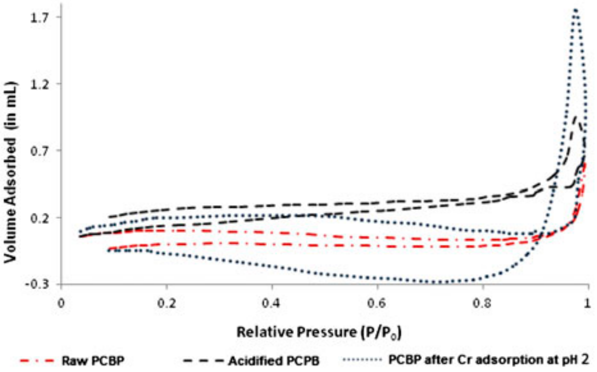

Fig. 8. BET adsorption behaviour of raw PCBP, acidified PCPB and PCBP after Cr adsorption at pH 2.

sample is 0.70 m^2/g. It is observed that the PCBP exhibits a type-II-III adsorption isotherm, indicating the macroporous nature of the sample [22]. Similar characteristics were observed for the acidified and Cr-treated PCBP. As shown in Table 1, a decrease in BET surface area, pore volume and average pore diameter was observed upon acidification of the PCBP. This could be explained by the increased hydrogen bonding in the sample due to the neutralization of the carboxylate group leading to strengthening of hydrogen bonding in the polymer which in turn leads to cross linking. However, upon Cr adsorption (500 mg/L aqueous solution of Cr(VI) at pH 2) onto PCBP, there was an increase in the BET surface area, with decrease in pore volume and average pore diameter in comparison with raw PCBP. This result indicates that the carboxylate neutralization is overweighed by the Cr reduction and adsorption under acidic conditions, and subsequently results in the change of the surface characteristics of the PCBP. Further, the Cr adsorption is evidenced by the decrease in the pore volume and the pore diameter due to the occupancy of the same by Cr(III) ions.

3.1.5. Elemental analysis

The elemental analysis (CHNS) of PCBP using Flash 2000 elemental analyzer revealed that it has 48.80% carbon, 6.27% hydrogen, and 0.71% nitrogen. Sulphur was not detected in the sample. But as the PCBP sample has 1.3% ash content; hence, a correction factor was applied to the results accordingly. Based on these results, the empirical formula of PCBP was derived from this elemental composition and it was found to be $C_{824}O_{542}H_{1270}N_{10}$. The C:N, O:C and H:C ratios for the PCBP were 68.67, 0.88, and 0.13, respectively. As these values lie in the first quadrant of Van Krevelen plot which suggests the organic sample to be that of biomass. There is a significant deviation in value of O:H for PCBP (0.43) from O:H for pure carbohydrates (O/H ratio = 0.5). This indicates the presence of lignin in the sample.

3.2. Batch adsorption studies

3.2.1. Effect of contact time

It is clear from Fig. 9 that in case of PCBP, the rate of Cr adsorption increased initially and then slowed down after 2 h of shaking. The results depicted that after 2 h contact time, there was 15.5% Cr removal. Further, only 5% increase in the Cr removal was observed on increasing the contact time to 24 h. During the 2 h contact time, the percent Cr adsorption by AC was found to be 17.1% which showed an increase

Table 1
Details of the cone biomass and its acid-treated and Cr-treated sample

S. No.	Material	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
1.	Raw PCBP	0.6988	0.000877	5.0187
2.	Acidified PCPB	0.3702	0.000327	3.5362
3.	PCBP after Cr adsorption at pH 2	0.8215	0.000756	3.6811

Table 2
Langmuir parameters for adsorption of Cr(VI) on PCBP

Adsorbent	Adsorption capacity (q_m) (mg/g)	Adsorption energy (b) (L/mg)	Correlation coefficient R^2
PCBP	250	0.032	0.985
AC	333.33	0.058	0.984

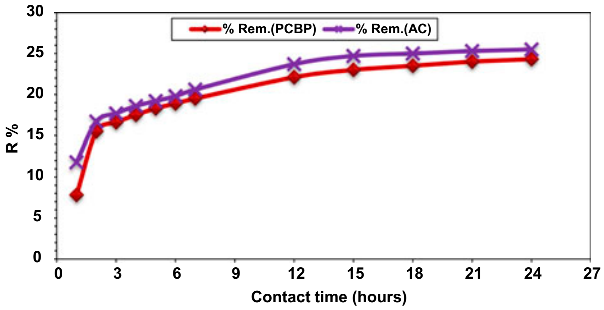

Fig. 9. Effect of contact time on Cr removal by AC and PCBP (initial ion conc. = 200 mg/L, adsorbent dose = 2 g/L, pH 4.5, shaking speed = 200 rpm, temperature = 25 ± 1 ℃).

of about 8.6% when the contact time was increased to 24 h. As the adsorption process was fast during initial 2 h and then become slow, so 2 h was selected as optimum time for further studies.

The increase in the adsorption during initial stages could be attributed to the diffusion of adsorbate ion through the fluid film around external surface of the adsorbent material, followed by diffusion of adsorbate ions to the internal pores of the adsorbent material. During the initial stages the concentration gradient between film and solid surface is large, which leads to fast mass transfer of Cr ions on the adsorbent surface [23]. Similar trend has also been reported in various studies [24–27].

3.2.2. Effect of pH

An increase in the percent Cr removal with decrease in pH of the solution was observed (Fig. 10). As the pH decreased from 5 to 1 for a given concentration of Cr, the removal efficiency increased from 18.5% to 81.9% and 25.8% to 96.8% in case of PCBP and AC, respectively.

The pH dependence of Cr adsorption can be attributed to the functional groups present on the surface of the protonated biomass. As the pH of Cr solution is varied, the equilibrium also shifts accordingly. Cr(VI) in the pH range of 1.0–5.0 co-exist in different forms, such as $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, and $Cr_4O_{13}^{2-}$ of which $HCrO_4^-$ is most predominant. With the decrease in the pH of aqueous solution, CrO_4^{2-} and $Cr_2O_7^{2-}$ become predominant species. On the contrary, at lower pH, protonation occurs on the adsorbent surface which results in significantly strong electrostatic attraction between positively charged adsorbent surface and negatively charged chromate ions [28–30]. On the other hand, with increase in pH, the degree of protonation of the adsorbent surfaces reduces slowly and hence removal efficiency decreases. At pH ≥ 5, lesser adsorption of Cr(VI) may be attributed to the competition among CrO_4^{2-} and OH^- ions on the surface of adsorbent [29,31,32].

Though CBP has maximum adsorption efficiency at pH 1 but the pH 1 solution is quite corrosive in nature. Hence, further experiments were carried out at pH 2.

3.2.3. Effect of adsorbent dose

Effect of PCBP and AC dosage on Cr(VI) adsorption was investigated using 200 mg/L Cr(VI) solution by changing the sorbent dose from 0.125 g/L to 6 g/L, at pH 2. The results showed an increase in the removal efficiency from 10.5 to 100% and 13.9 to 100% in case of PCBP and AC, respectively, upon increasing the dose of adsorbent from 0.125 g/L to 6 g/L (Fig. 11). With the increase in the adsorbent dose,

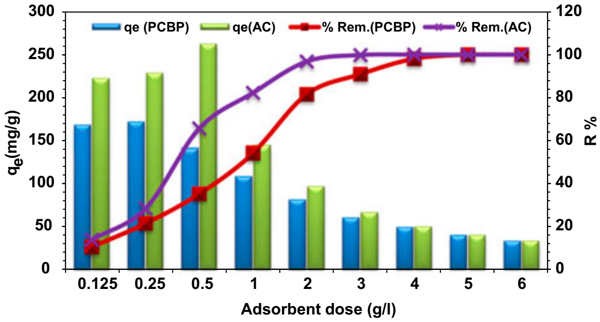

Fig. 10. Effect of pH on percent Cr removal and its uptake (initial ion conc. = 200 mg/L, adsorbent dose = 2 g/L, temperature = 25 ± 1℃, contact time = 2 h, shaking speed = 200 rpm, equilibrium time = 22 h).

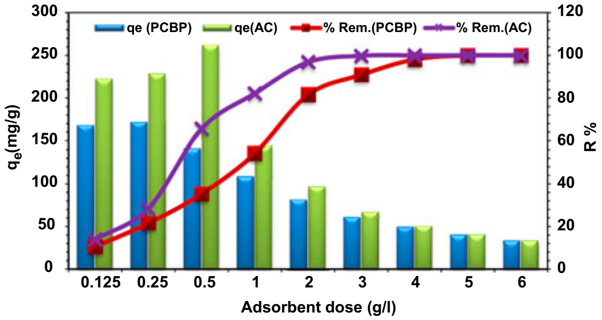

Fig. 11. Effect of adsorbent dose on percent Cr removal and its uptake (initial ion conc. = 200 mg/L, pH 2, shaking time = 2 h, shaking speed = 200 rpm, equilibrium time = 22 h, temperature = 25 ± 1℃).

percent Cr removal was increased while its uptake (q_e) was decreased. This may be accounted to the limited availability of sorption site at low PCBP dose as compared to the large amount of Cr(VI) in solution, resulting in a low removal efficiency. With the increase in the dose, the number of available sorption sites became sufficient and resulted in better removal of Cr [27,33].

However, an increase in the Cr(VI) uptake (q_e) was observed when adsorbent dose increased from 0.125 g/L to 0.25 g/L in case of PCBP and from 0.125 g/L to 0.5 g/L in case of AC. But in both cases, further increase in adsorbent dose leads to decrease in Cr(VI) uptake (q_e). This may be attributed to the fact that at higher adsorbent dose lesser Cr ions were available per unit mass of the adsorbent and the active sites on the adsorbent surface remained unsaturated [27]. A similar trend of increase in the Cr(VI) removal percent and decrease in the Cr uptake (q_e) with increasing the adsorbent dose was reported in other studies also [34,35].

3.2.4. Effect of initial ion concentration

The effect of initial Cr(VI) concentration on the adsorption efficiency was studied at pH 2 and adsorbent dosage of 0.25 g/L (Fig. 12). The results indicate that the percent Cr(VI) removal decreased with increasing adsorbate concentration. The percent Cr removal decreased from 34.7 to 8.6% and 44.5 to 10.9%, when initial concentration was increased from 100 mg/L to 600 mg/L Cr(VI) for PCBP and AC, respectively. This may be due to the fact that the number of active adsorption sites to accommodate Cr remains constant, and hence, the percent removal efficiency by adsorption decreases [27].

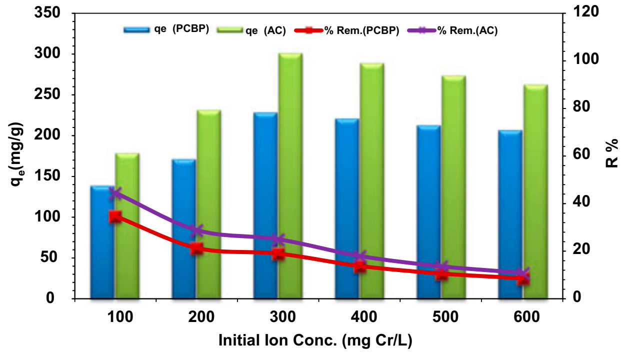

Fig. 12. Effect of initial ion concentration on percent Cr removal and its uptake (adsorbent dose = 0.25 g/L, pH 2, contact time = 2 h, shaking speed = 200 rpm, temperature = 25 ± 1°C, equilibrium time = 22 h).

Conversely, Fig. 12 also shows that the Cr uptake by AC increased with the increase in initial Cr(VI) concentration up to 300 mg/L. This is because further addition of Cr(VI) to the solution led to the complete utilization of adsorption sites of the adsorbent material. But once the adsorption sites got saturated, further increase in the Cr(VI) lead to no significant uptake [27,36].

3.3. Development of isotherm

The Langmuir isotherm model was applied to study the effect of initial Cr(VI) concentration on adsorbate uptake using both PCBP and AC. The equilibrium adsorption data for both PCBP and AC fitted excellently to Langmuir isotherm model and provided linear fit diagrams of Langmuir adsorption model (Fig. 13), with good correlation of 0.985 and 0.984 for PCBP and AC, respectively. The monolayer adsorption of Cr(VI) on the adsorbent surface was confirmed by high correlation coefficient. Values of q_m, adsorption energy (b) and dimensionless factor (R_L) were determined from these linear fit diagrams (Table 2). The adsorption capacity to form a monolayer (q_m) was found to be 250 and 333.33 mg/g for PCBP and AC, respectively. Adsorption energy (b) was 0.032 L/mg for PCBP and 0.058 L/mg for AC, respectively. Separation factor R_L was found to lie between 0.05 to 0.32 for PCBP and 0.03 to 0.24 for AC. In both the cases, value of R_L lies between 0 and 1, which indicate favourable adsorption of Cr onto PCBP and AC.

3.4. Adsorption kinetics

Adsorption data of the contact time variation experiment was fitted in the Lagergren pseudo-first order, pseudo-second order, zero order, first-order

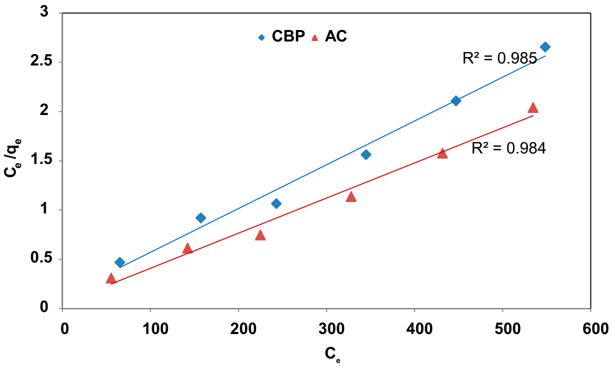

Fig. 13. Langmuir adsorption isotherm for PCBP and AC.

and second-order adsorption kinetic model, and it has been found that the pseudo-second-order adsorption kinetic model is best fit to the data. Fig. 14 presents the linear fit diagram of Lagergren pseudo-second-order adsorption kinetic plot for PCBP with high correlation coefficient of 0.998. The value of q_e drawn for the same model is in agreement with experimental q_e for PCBP and the value of pseudo-second-order reaction rate constant ($k_{2,\text{ads}}$) drawn from the plot is 0.018 min^{-1}.

3.5. Adsorption thermodynamics

The adsorption characteristics of PCBP were carried out at different temperatures (288, 298, and 308 K). The adsorption efficiency at these temperatures was used to deduce the thermodynamic equilibrium constant (K_c) and Gibbs free energy of adsorption (ΔG) for adsorption using Eqs. (7) and (8). The results of the derived thermodynamic parameters are shown in Table 3.

Further, the value of heat of sorption (ΔH) and standard entropy (ΔS) were determined from the slope and intercept of plot ΔG vs. T (Fig. 15) and found to be 4.014 kJ/mol and 0.024 kJ/mol/K, respectively. The negative value of ΔG indicated that the adsorption of Cr(VI) on PCBP is spontaneous in nature while it is favoured by an increase in the entropy with an endothermic physisorption phenomenon.

3.6. Ashing studies of PCBP

The ashing of the sample of raw PCBP and Cr-adsorbed PCBP was carried out, and the ash yield were found to be 1.3 and 11.0%, respectively. This indicates a significant adsorption of Cr onto the PCBP material.

Table 3
Thermodynamic parameters for adsorption of Cr(VI) on PCBP at different temperature

Temperature (K)	K_c	ΔG (kJ/mol)
288	3.512195	−3.00798
298	3.753086	−3.27678
308	3.917012	−3.49621

Further, comparison of AC with PCBP material shows lower q_e, attributed to the lesser surface area. On the other hand, it is well known that AC is formed under pyrolytic conditions from wood in the presence of activators as additives [37]. Thus, the AC is only about 20% by weight of biomass utilized. This means that on biomass to biomass comparison, the adsorption efficiency of charcoal at say 20% yield will be 66 mg/g, which is an order lower than the q_e of PCBP. Thus, the PCBP material is a better and cost-effective sorbent for Cr as compared to AC. Further, ashing would be a suitable method for the management of the waste generated followed by recovery of Cr.

3.6.1. Comparison with other low-cost adsorbents

An account of the various bio-waste materials explored for Cr removal from effluents along with their metal uptake efficiency (q_e (mg/g)) has been listed in Table 4. It reveals that metal uptake efficiency (q_e (mg/g)) of PCBP is very high as compared to other bio-waste materials. The results are in agreement with the results reported in a previous study where cone biomass of *Pinus sylvestris* has shown metal ion uptake efficiency of nearly 202 mg/g [26].

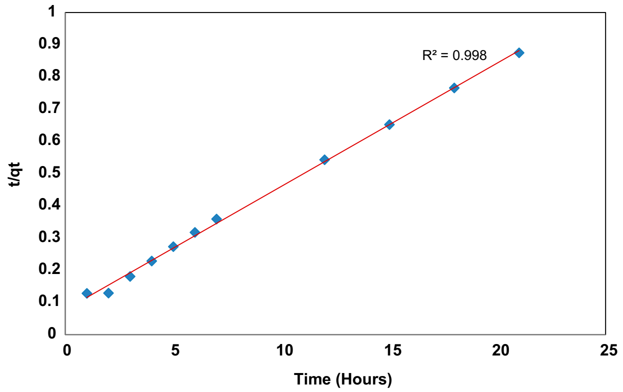

Fig. 14. Lagergren pseudo-second-order adsorption kinetic plot for adsorption of Cr(VI) on PCBP.

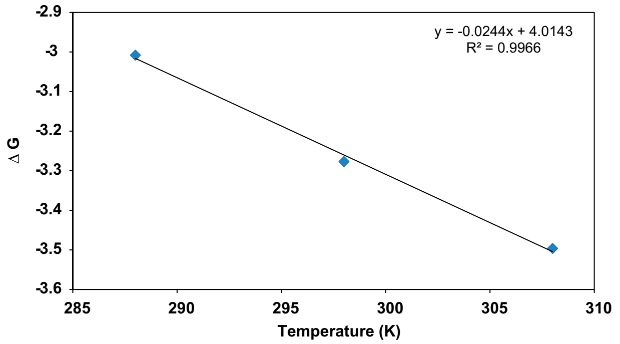

Fig. 15. Plot of Gibbs free energy of adsorption (ΔG) vs. temperature for adsorption of Cr(VI) on PCBP.

Table 4
List of various bio-waste materials explored for Cr removal from effluents

S. No.	Bio-waste source	Range of initial concentration of Cr(VI) (mg/L)	Amount of adsorbent used (g/L)	Metal uptake q_e (mg/g)	References
1	*C. vulgaris*	36.1–263.0 (263.0)*	1	33.8	[38]
2	*S. obliquus*	28.1–230.4 (230.4)*	1	30.2	[38]
3	*Synechocystis* sp.	29.9–237.3	1	39.0	[38]
4	Almond Husk	20–100 (100)*	50	1.65	[39]
5	Pine needles	20–1,000	8	21.50	[40]
6	Almond shells	20–1,000	8	10.616	[40]
7	Cactus leaves	20–1,000	8	7.082	[40]
8	*Dunaliella* sp. 1	56.6–272.4 (272.4)*	1	102.5	[41]
9	*Dunaliella* sp. 2	47.7–255.0 (255.0)*	1	85.5	[41]
10	Cone biomass of *Pinus sylvestris*	50–300 (300)*	1	201.80	[26]
11	London plane leaves	52.82–315.58 (315.58)*	2	69.47	[42]
12	Apricot stone	20–300	–	58.86	[43]
13	Almond shell	20–300	–	59.64	[43]
14	Cornelian cherry	20–300	–	59.40	[43]
15	Hazelnut shell	50–300 (300)*	2.5	92	[44]
16	Vegetative cell cultures of *B. thuringiensis*	25–250 (250)*	1	54.7	[45]
17	Spore–crystal mixture of *Bacillus thuringiensis*	25–250 (250)*	1	61.5	[45]
18	*Mucor hiemalis*	10–600 (600)*	1	41.8	[46]
19	Pomegranate husk	25 and 50 (25)*	5	10.59	[47]
20	Tamarind fruit shell	50–200 (200)*	1	74.62	[48]
21	*Azadirachta indica* (neem) leaf powder	25–125 (125)*	1	4.92	[49]
22	Neem leaves	40–700 (700)*	10	62.97	[50]
23	Boiled rice husk	10–70 (70)*	4	6.39	[51]
24	Boiled saw dust	10–70 (70)*	4	8.87	[51]
25	Maize bran	200–300 (300)*	20	13.56	[52]
26	Coconut coir pith	20 to 100 (100)*	1	65.2	[34]
27	Wheat bran	2.5–15 (5)*	20	0.942	[53]
28	Reed biomass	5–1,000 (1,000)*	4	42.6	[54]
29	*Citrus reticulata* (kinnow) waste biomass	25–800 (800)*	1	195	[55]
30	Tamarind seeds	40–400 (400)*	10	27.5	[56]
31	*Posidonia oceanica* fibres	5–50 (50)*	10	2.4	[57]
32	*Nymphaea rubra*	20–100 (100)*	1	79.8	[58]
33	Mango sawdust	10–150 (150)*	2	37.73	[59]
34	Neem sawdust	10–150 (150)*	2	58.82	[59]
35	Orange peel	10–150 (150)*	2	19.80	[59]
36	Sugarcane bagasse	10–150 (150)*	2	23.8	[59]
37	Wheat shell	10–150 (150)*	2	28.08	[59]
38	Walnut hull	240–480 (480)*	5	90.8	[60]
39	Sugarcane pulp residue	10–60 (60)*	33	0.567	[61]
40	Maize tassel	25–500 (400)*	10	10	[10]
41	Corn husk	20–260 (200)*	2.5	7.59	[62]
42	Pine needles powder	50–400 (400)*	10	40	[63]
43	*Arachis hypogea* shells	5–500 (500)*	15	31.26	[64]
44	*Psidium guajava* leaves powder	22.5–180 (180)*	40	1.64	[65]
45	Coconut coir	10–500 (500)*	2	70.4	[66]

(*Continued*)

Table 4 (*Continued*)

S. No.	Bio-waste source	Range of initial concentration of Cr(VI) (mg/L)	Amount of adsorbent used (g/L)	Metal uptake q_e (mg/g)	References
46	Chestnut shell	25–200 (200)*	20	7.96	[67]
47	*Ficus carica* fibre	50–500 (350)*	5	13.41	[68]
48	*Strychnos potatorum* Seed	10–250 (250)*	20	59	[69]
49	*Spirulina* sp.	10–50 (50)*	1	34.56	[70]
50	*Citrus limetta* peel	25–65	30	3.9	[71]
51	Orange peel powder	50–500 (500)*	10	5.27	[72]
52	Cone biomass of *Picea smithiana*	300–600 (300)*	0.25	228	Current study

*Initial ion concentration (mg/L) at which maximum adsorption occurred per gram of adsorbent.

4. Conclusion

The development of cost-effective and efficient adsorbent materials for the removal of Cr(VI) from contaminated water is imperative where environment and human health is concerned. From the experimental results, it can be concluded that PCBP has excellent adsorption affinity for Cr(VI) from aqueous solution in comparison with the AC. Separation factor R_L value calculated for PCBP and AC indicates that the adsorption of Cr(VI) on PCBP and AC was thermodynamically favourable. Being easily available, free of cost and having almost no significant use except for burning by local people, it is a suitable alternate and a low-cost adsorbent for Cr(VI) removal from the aqueous solutions.

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