Removal of Chromium(VI) Using Chemically Activated Pistachios Seed Shell Carbon and Commercially Available Carbon

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Abstract: Pistachios seed shell carbon and commercially activated carbon was used for the removal of heavy metals from industrial wastewater have been studied. Pista seed shell carbon is a natural, low cost and eco-friendly adsorbent. Pistachios seed shell carbon was used for the removal of Cr(VI) from synthetic water. The carbon characteristics was determined by moisture content, ash content, matter soluble in both water and acid, range of pH, decolourising power, iron content, ion exchange capacity and zero point charge. The adsorbents were tested by using batch experiments under controlled conditions. The effect of various experimental parameters were examined such as equilibrium time, function of pH, adsorbent dose, concentration, temperature, agitation speed, various adsorbent size were investigated. The obtained equilibrium adsorption data is fitted to the linear forms of Freundlich, Langmuir, Temkin adsorption isotherms. The carbon was characterized by x-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FT-IR) before and after adsorption. These results indicate that PSSC is a very good adsorbent than CAC and it can be used for the development of highly efficient adsorbent for the separation of heavy metals from synthetic water.

Introduction

Every organism is surrounded by materials and forces which contribute its environment, from which it must be, derive its needs. Environment creates favourable conditions for the existence and development of living organisms[1]. Any unit that includes all of the organisms in a given area interacting with the physical environment so that a flow of energy leads to clearly defined trophic structure, biotic diversity and material cycles within the system is an Environment[2]. The unfavourable alteration of our surroundings" is known as environmental pollution**.** It changes the quality of air, water and land which interferes with the health of human and others life on earth[1]. A toxic heavy metal is any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts[3].

Water-insoluble chromium(III) compounds and chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of chromium(VI) have been known for a long time[4]. Over exposure to chromium can occur in welders and other workers in the metallurgical industry, persons taking chromium-containing dietary supplements, patients who have received metallic surgical implants and individuals who ingest chromium salts[5]. The increase in removal efficiency with contact time is due to increase in surface area and hence more active sites are available adsorption[6]. In recent years there are available methods that have been used for advanced wastewater treatment. These are adsorption, chemical oxidation, desalination, chemical coagulation and filtration, *etc*. The purpose of carbon adsorption is also to remove organic as well as inorganic components in the wastewater. This process aims to compare the capacity of bio-adsorbent with the commercially available carbon, for removal of nickel, a toxic heavy metal from wastewater by the method of adsorption. Pistachios seed shell carbon (PSSC) and commercially activated carbon (CAC) are used for the removal of Cr(VI) from synthetic water.

Experimental

Pistachios seed shell were collected for sufficient quantity and treated with concentrated hydrochloric acid. The material was kept for 24 hours to facilitate charring of material. They were washed with distilled water to remove free acid and in distilled water for several times. And then added a 10% NaOH solution and kept for an hour and then filtered. After filtration it was washed with distilled water for several times. It is then dried in a hot air oven at 110 ºC for 3 hours. The second adsorbent used for systematic studies was the commercially available carbon got from precision scientific company.

Spectronic-20-Spectrophotometer

The spectronic-20-spectrophotometer was used to measure the relative amount of light transmitted, yielding results in transmittance. It is a single beam spectrometer with an overall wavelength range of 340 nm to 950 nm.

Characterization of PSSC and CAC
Physicochemical characterizations of both carbons

The capacity of bio-adsorbent with the commercially available carbon, for removal of chromium, a toxic heavy metal from wastewater by the method of adsorption. Pistachios seed shell carbon (PSSC) and commercially activated carbon (CAC) were used for the removal of Cr(VI) from synthetic water. The characteristics were determined for PSSC and CAC by moisture content, ash content, matter soluble in both water and acid, range of pH, decolourising power, iron content, ion exchange capacity and zero point charge (Table 1).

Batch mode studies

Batch experiments were carried out which included effect time, effect of pH, effect of carbon dosage, to estimate the percentage of chromium adsorbed by both the adsorbents separately. These studies were further verified with Freundlich adsorption isotherm. Regeneration studies were carried out to recover the metal and adsorbent.
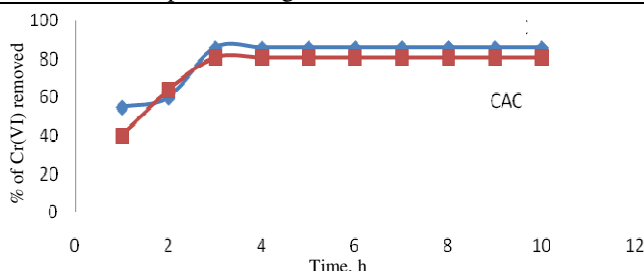
Results and Discussion
Effect of equilibrium time

Figure 1 shows the effect of equilibrium time on the removal of Cr(VI) by PSSC and CAC. The removal increases with increase in time and attains equilibrium at third hour for PSSC and CAC respectively. The percentage of removal for PSSC are found to be 86 and 81 for CAC.

Table 1. Physicochemical characteristics of PSSC and CAC

S.No	Characteristics	PSSC	CAC
1.	Moisture content, %	43.74%	7.869%
2.	Ash content, %	27.062%	4.2955%
3.	Apparent density, g/cc	0.7592 g/cc	0.1877g/cc
4.	Matter soluble in water, %	11.084%	15.2242%
5.	Matter soluble in acid, %	11.546%	9.5082%
6.	pH	4.75	7.93
7.	Decolourising power, mg/g	210 mg/g	6 mg/g
8.	Iron content, %	15%	50%
9.	Ion exchange capacity	0.03	NIL
10.	Zero point charge	5.3	6.5

Figure 1. Effect of equilibrium time on the removal of Cr(VI)

Effect of initial concentration

Figure 2 shows the effect of various concentration on the removal of Cr(VI) by PSSC and CAC. The removal increase with increase in the various concentration and it attains the highest removal concentration as 10 ppm for PSSC and CAC. The maximum percentage of removal for chromium by PSSC are found to be 81 and 76 for CAC.
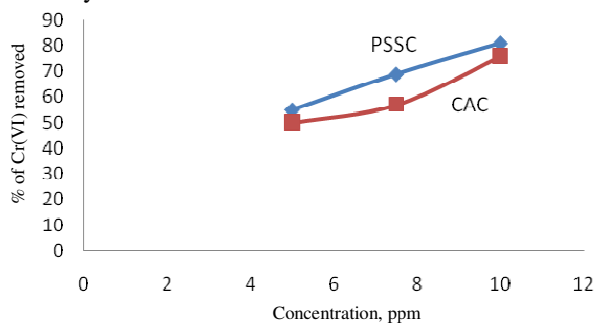
Figure 2. Effect of initial concentration

Effect of pH

Figure 3 shows the effect of pH on the removal of chromium by PSSC and by CAC with increase in pH, the percentage removal increases and reaches the maximum at pH 2 and 4. The percentage of nickel removed by PSSC is higher by 83% than that of CAC 72%. The influence of pH on the removal of chromium may be explained as follows: A pure carbon surface was considered non-polar, but as the pH increases the adsorbent surface becomes more and more negatively charged and adsorption of Cr(VI) is more favourable.
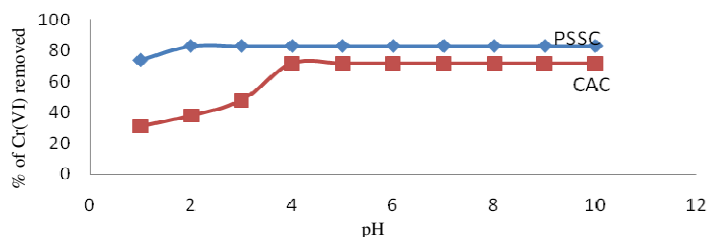
Figure 3. Effect of pH

Effect of carbon dosage

Figure 4 clearly reveals that the carbon dosage used for removal of chromium using PSSC and CAC which represents the removal of chromium as a function of carbon dosage by PSSC and CAC respectively. It shows that for quantitative removal of chromium from 100 mL of solutions containing mg/L. Chromium is a minimum dose of 200 mg of PSSC was required, but for CAC is a minimum dose of 250 mg was required. The increase in adsorption with increase in adsorbent dose is due to increase in the surface area of the adsorbents and hence more active sites are available for the adsorption of the metal ion[7].
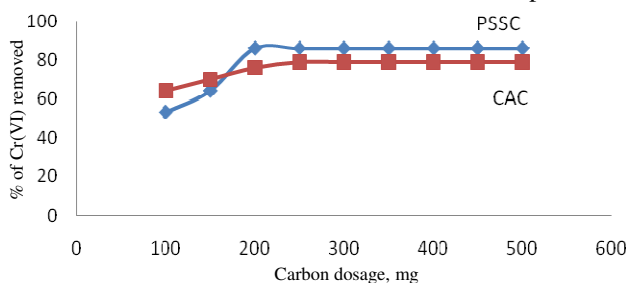
Figure 4. Effect of carbon dosage

Effect of particle size

Figure 5 shows the lower particle size showed maximum adsorption which maybe due to the availability of larger surface area. Activated carbon has larger surface area (smaller particle size) than carbon (larger particle size). The removal efficiency of Cr(VI) ions by PSSC and CAC through different sizes. It can be observed that the maximum adsorption efficiency is achieved with particle size 75-150 µm for PSSC and >75 µm for CAC. There is a decrease in adsorption efficiency when the particle size is greater. This may be due to the lack of availability of adsorption sites. Smaller particle size showed maximum adsorption, which may be due to the availability of a larger surface area[8].
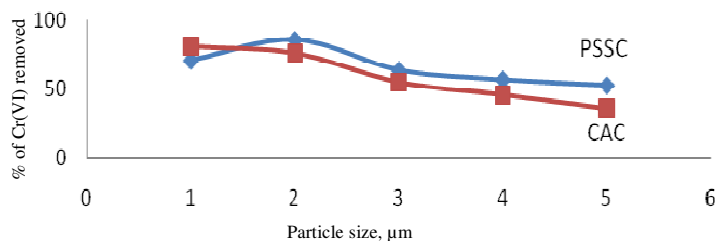

Figure 5. Effect of particle size

Effect of agitation speed

Figure 6 shows the agitation speed less than 120 rpm favours the maximum removal of

Cr(VI) by both PSSC and CAC. The maximum removal of Cr(VI) ions takes place at 100 rpm for Cr(VI) ions onto both PSSC and CAC.
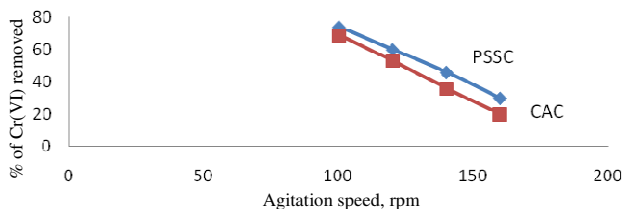

Figure 6. Effect of agitation speed

Figure 7 shows the sorption of Cr(VI) ions from metal ion solution using the adsorbents like PSSC and CAC were carried out the temperature ranges of 20^0-60 ^{o}C. At low temperatures, the mobility of the metal ions in aqueous solution maybe low; hence, minimum amount of metal ions get removed especially at 30 ^{o}C.
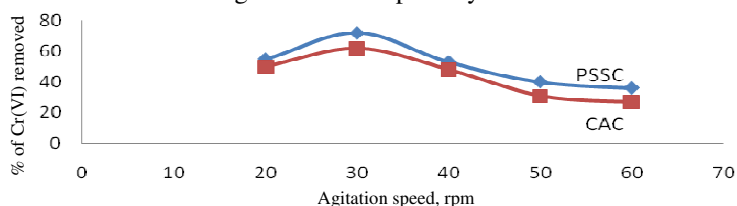

Figure 7. Effect of temperature

Effect of temperature

Freundlich adsorption isotherm for PSSC and CAC

Figures 8 and 9 show that Freundlich equation was used to check the effect of adsorption. This equation was useful as a means of data description. Freundlich adsorption isotherm which is the form

$$\log (x/m) = \log k + 1/n \log C_{eq}$$

k = Equilibrium constant

C_{eq} = equilibrium concentration

x/m = amount adsorbed per unit mass

The log (x/m) values are plotted against log C_{eq}. The straight line nature of plots indicate that the process follows obey Freundlich adsorption isotherm. The k values of Freundlich equation was obtained for PSSC and CAC from intercept in the log x/m axis. The sorption intensities (1/n) were obtained for both the carbons from the slopes of the straight line curves. The k values were found to be 0.2 and 0.3 for PSSC and CAC respectively. The values of n were calculated for both the carbons. The values of 1<n<10 shows favourable adsorption of nickel on both the carbons. The 'n' values are calculated as 1.2 and 2.5 for PSSC and CAC respectively, which shows that both are having good adsorption capacity.
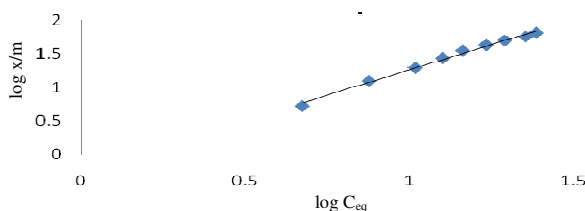

Figure 8. Freundlich adsorption isotherm for PSSC
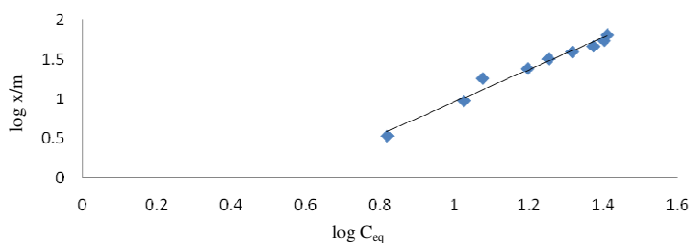
Figure 9. Freundlich adsorption isotherm for CAC

Langmuir adsorption isotherm for PSSC

Langmuir isotherm (Figure 10 & 11) governs the monolayer coverage of the adsorbent on the surface of the adsorbent. Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is applicable for monolayer sorption onto a surface containing a finite range of indistinguishable sites.

The model assumes uniform energies of sorption onto the surface and no transmigration of adsorbate within the plane of the surface. It is represented as $C_e = 1/Q_o b + C_e/Q_o$

C_e = The equilibrium concentration of the metal ion, mg dm^{-3}

Q_e = The amount of metal ion adsorbed at equilibrium, mg g^{-1} and Q_o and b are Langmuir constants. A graph was drawn by plotting $1/x/m$ *vs.* $1/C_{eq}$
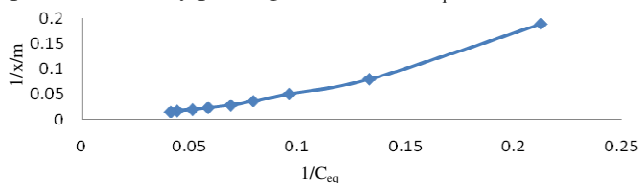

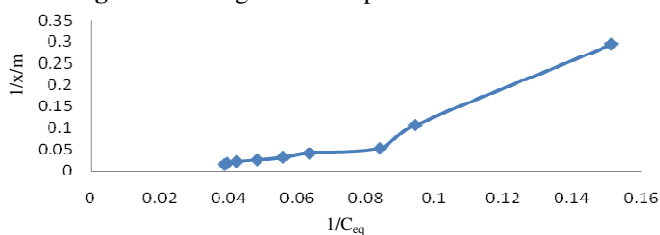**Figure 10**. Langmuir adsorption isotherm for PSSC

Figure 11. Langmuir adsorption isotherm for CAC

Temkin adsorption isotherm

The adsorbent- adsorbate interactions were studied by the Temkin isotherm (Figure 12 & 13). By ignoring the extremely low and large values of concentration, the model assumes that the heat of ion exchange/adsorption of all molecules in the layer would increase linearly rather than the logarithmic with coverage. Its derivation is characterized by a uniform distribution of binding energies which was carried out by plotting the quantity adsorbed x/m against ln C_{eq}.

Regeneration studies

Regeneration studies help to elucidate the adsorption nature and to recover metals from water and adsorbent. Attempts were made to regenerate nickel from the adsorbent carbons using HCl of various strengths ranging from (0.01-0.10 N). It has been found that concentration of 0.01 N of HCl was required to recover 77% of PSSC and 75% of CAC respectively.
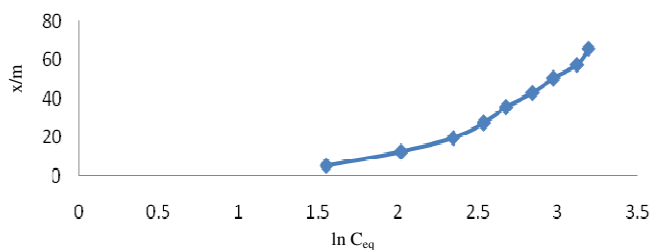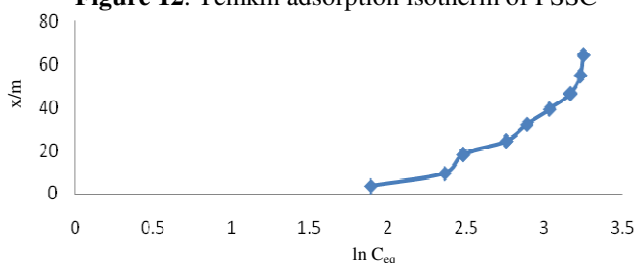
Figure 12. Temkin adsorption isotherm of PSSC

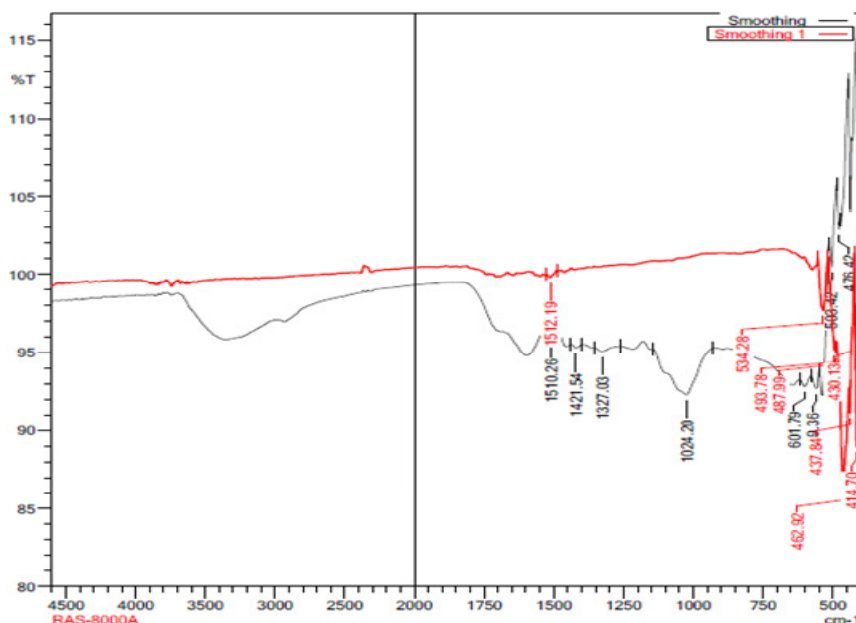**Figure 13.** Temkin adsorption isotherm of CAC

Figure 14. FT IR spectrum of PSSC before and after adsorption

FT-IR spectrum of CAC before and after adsorption

Figures 14 & 15 show the FT-IR spectrum of PSSC and **CAC** before and after adsorption. The intense band of this figure clearly explains the high adsorption capacity of PSSC and **CAC.** Spectrum (Figure 14) show the presence of many functional groups which is present in PSSC before and after adsorption. The frequency observed at 1510.26 cm^{-1} and 1512.19 cm^{-1} are due to the presence of nitro compounds N-O assymmetric stretching. The frequency observed at 601.79 cm^{-1}, 534.28 cm^{-1} may be due to the presence of alkyl halides or Halo

alkanes. Spectrum (Figure 15) shows the presence of many functional groups which is present in **CAC** before and after adsorption. The frequency observed at 599.86 cm^{-1}, 555.40 cm^{-1} and 557.50 cm^{-1} due to the presence of Alkyl halides like C-Cl, C-Br and C-I stretching. Figure 15 spectrum show the frequency observed at 3400-1600 cm^{-1} may be due to the stretching and bending vibration of H_2O molecule. Shifting of frequency could not be observed for the PSSC and CAC before and after adsorption. From this we can conclude the functional groups have not been changed for PSSC and CAC before and after adsorption.
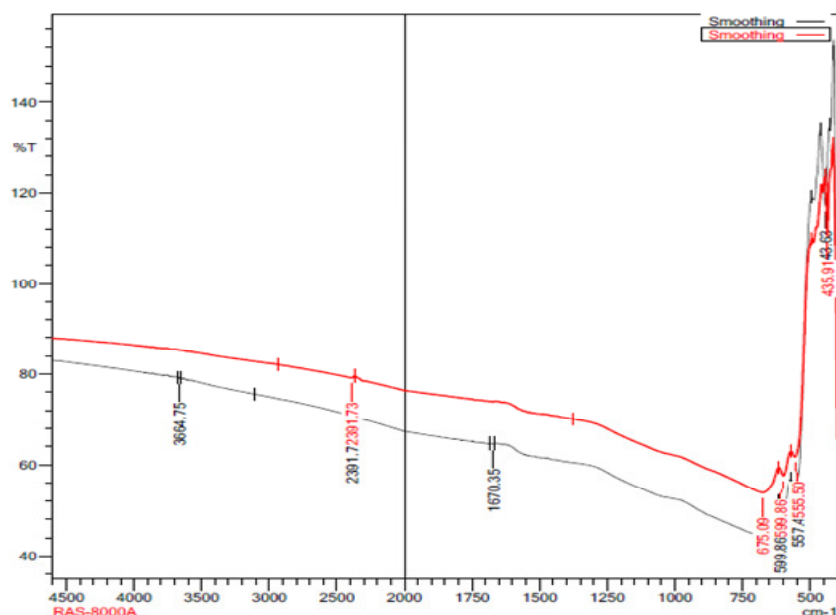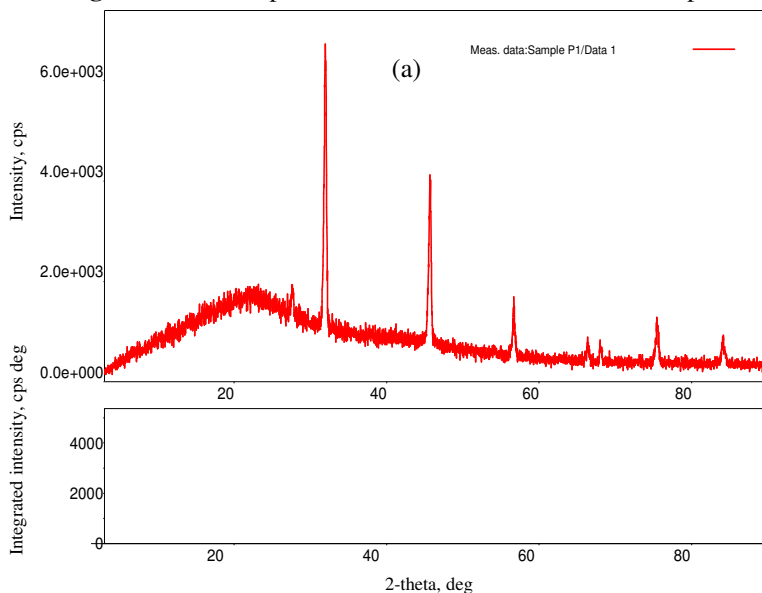

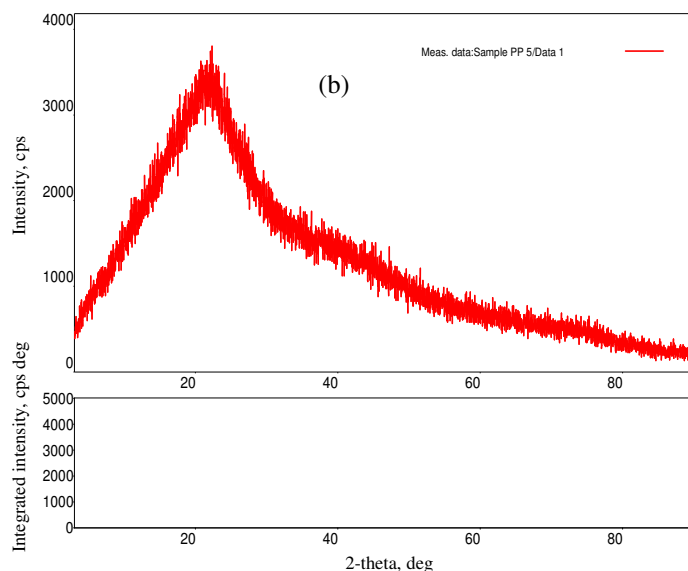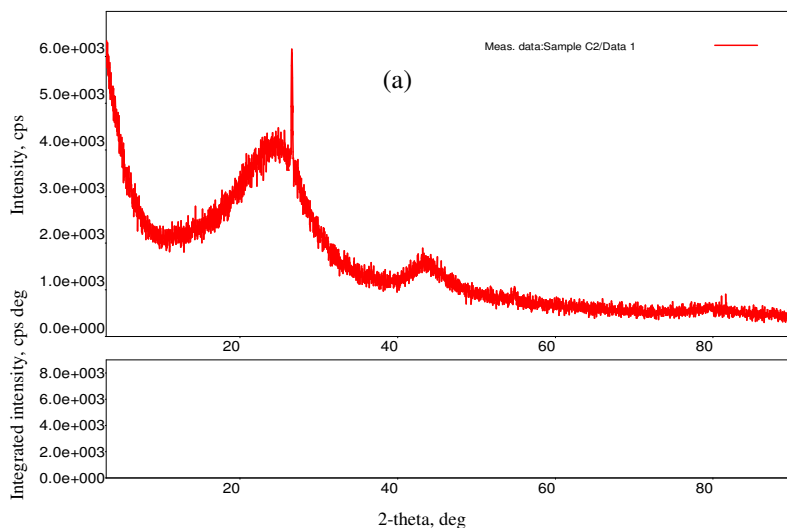**Figure 15.** FT IR spectrum of CAC before and after adsorption

Figure 16. X-ray diffraction spectrum of PSSC before (a) and after (b) adsorption

The XRD pattern of PSSC and CAC for before and after adsorption is shown in Figures 16(a,b) & 17(a,b) there was significant difference observed in Chromium adsorbed PSSC & CAC compared to non-adsorbed PSSC & CAC. Cr(VI) adsorbed PSSC & CAC showed higher intensity of diffraction peaks.

The increment in the crystallite size is may be due to increment in space charge polarization and crystal defects after adsorption. The literature of carbon materials repeatedly refers to the crystal and to the crystal size, with its graphitic connotations, in analyses of structure within activated carbon based on XRD data. The crystalline structure increases the adsorption of metals on to prepared activated carbon, where the metals adsorbed on the upper layer of the crystalline structure of the carbon surface by means of physisorption.
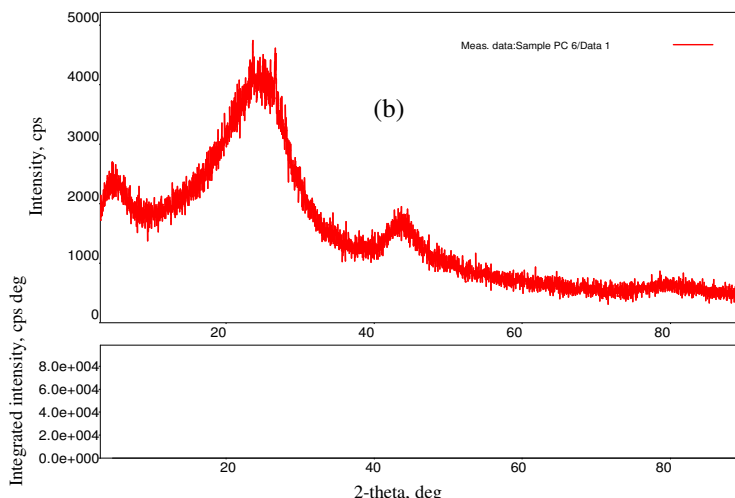
Figure 17. X-ray diffraction spectrum of CAC before (a) and after (b) adsorption

Conclusion

Investigation from the above studies using the adsorbent as PSSC and CAC, the following conclusions were drawn, since the preparation of PSSC was much easier and pista seeds are abundantly available ass unwanted material, this seed is preferred for the study. From the study of characteristics of PSSC and CAC, PSSC was found to be a better adsorbent. By the batch mode studies it has been concluded that PSSC is better than CAC. Thus it can be concluded that PSSC is economically reliable, cheaper and effective adsorbent in the removal of nickel from wastewater of chemical industries compared to CAC.

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