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RESEARCH ARTICLE

Adsorptive Removal of Cd(II) from Aqueous Solutions Using Chemically Activated Pistachios Seed Shell and Commercially Activated Carbon

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Abstract: The capacity of hydrochloric acid treated pistachios seed shell carbon (PSSC) for the removal of cadmium from aqueous solution was examined. The effect of various experimental parameters such as equilibration time, pH, carbon dosage, temperature, agitation speed, particle size was studied using batch process. The experiment demonstrated showed that the equilibrium adsorption data fit the Freundlich adsorption isotherm. The adsorbents used in this study are characterized by FT-IR, XRD before and after adsorption of cadmium ion. Desorption study was carried out using HCl solution with a view to regenerate the spent adsorbent and to recover the adsorbed metal ion. The result obtained clearly indicates that PSSC is a very good adsorbent than commercially activated carbon (CAC) and it can be used for the removal of heavy metals from synthetic water.

Keywords: Adsorption, Pistachios seed shell, Commercially available carbon, Isotherm, Desorption

Introduction

Due to rapid industrialization and urbanization, heavy metal pollution is a serious problem today. Most of these heavy metals do not undergo biological degradation, resulting into harmless end products[1]. Toxic heavy metals are found naturally in earth and become concentrated as a result of human activities[2]. Cadmium, zinc, copper, nickel, lead, chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities smelting, manufacture of batteries, tanneries, petroleum refining, paint manufacture, printing industries[3]. The high concentration of cadmium, a toxic heavy metal is very dangerous for human being and ecosystem. It can be released to the environment from many kinds of industrial activities such as ceramics, metal plating, textile[4]. Adsorption is a highly effective and economic technique for the removal of heavy metals from waste stream. Therefore eco-friendly and cost effective new technologies are required for the removal of heavy metals from waste streams by appropriate treatment before releasing into the water bodies[5]. Natural material of certain waste from industrial or agriculture is one of the resources for low cost adsorbents. These materials are locally and easily available in large quantities. Therefore, they are inexpensive and have less economic value[6]. Many adsorbents are proved to be efficient in removing excess metal concentrations from aqueous medium. In the present study pistachio seed shell powder was used as an agricultural waste adsorbent and its removal capacity of Cd(II) from ground water is investigated.

Experimental

All the chemicals used in the study were of analytical grade. Distilled water was used for the performance of batch experiments throughout the study. Testing of cadmium concentrations was performed using Spectronic-20-spectrophotometer.

Spectronic-20-spectrophotometer

The spectronic 20 spectrophotometer measures the relative amount of light transmitted, yielding results in transmittance, it is a single beam spectrophotometer with an overall range of 340 nm to 950 nm.

Adsorbent preparation

Pistachios seed shell powder were carbonized using 20 mL of concentrated hydrochloric acid, to get sufficient quantity of carbon for systematic studies of cadmium removal. After mixing the material were kept for 24 hours to facilitate charring. They were then washed free from acid using tap water and finally with distilled water, then added with a 10% NaOH solution and kept for an hour and then filtered. After filtration it was washed with distilled water several times. It is then dried a hot air oven at 110 ºC for 3 hours. The second adsorbent used for systematic studies was the commercially available carbon got Easwar chemicals.

Preparation or cadmium stock solution

The solution was prepared by dissolving 0.2854 g of $CdSO_4$ (3 $CdSO_4$. $8H_2O$) in water and diluted to 250 mL.

Batch experiments

Batch mode adsorption studies were carried out by agitating 10 ppm of cadmium(II) solution at desired concentration with different dosage of adsorbent. The samples were filtered and finally 2.5 mL of citrate buffer, KI, pyronine G solution and 1 mL of gelatin were added to the filtrate and analysed by spectrophotometer. Effects of equilibration time, adsorbent dosage, pH, particle size, temperature. Adsorption isotherm and desorption studies were also carried out.

Results and Discussion

Characteristics of the adsorbents

The characteristics of PSSC and CAC are presented in Table 1. It was observed that the hydrochloric acid treated Pistachio seed shell carbon and commercially activated carbon (CAC). The moisture content of PSSC and CAC was found to be 43.74% and 7.869% respectively. The ash content was estimated to be 27.062% and 4.2955% respectively whereas iron content was found to be 15% and 50% respectively. The matter soluble in acid and water for PSSC and CAC was found to be 11.546%, 9.5082%, 11.084% and 15.2242% respectively. The decolourising power of PSSC was 210 mg/g whereas for CAC was 6 mg/g.

Effect of equilibration time

Effect of contact time was studied by taking 10 ppm cadmium solution with an adsorbent. Rate of uptake of Cd(II) was initially higher and reached a steady value after reaching equilibration at 2nd and 4th hour for PSSC and CAC. The removal percentage was found to be 94 for PSSC and 91 for CAC (Figure 1). The increase in removal efficiency with contact time is due to increase in surface area and hence more active sites are available adsorption[7].

Table 1. Characterization data of carbon sample

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	0.1877 g/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	Decolorising power mg/g	210 mg/g	6 mg/g
8	Iron content, %	15%	50%
9	Ion exchange capacity	0.03	NIL

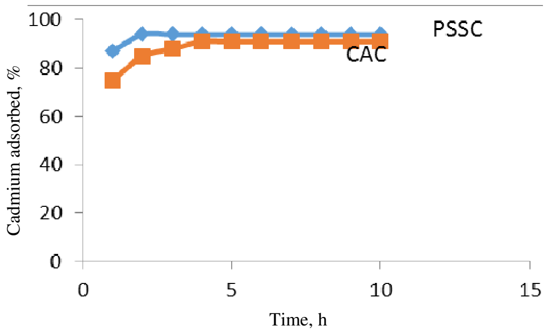

Figure 1. Effect of equilibrium time

Effect of pH

The influence of pH of the synthetic effluent on the extent of adsorption of cadmium(II) was carried out. The percentage of adsorption of the metal increases with increase in pH. Maximum removal was observed at pH 5.0-10.00 for PSSC and at pH 6.0-10.00 for CAC (Figure 2). At higher pH the reduction in adsorption may be possibly due to the abundance of OH^- ions creating increased hindrance to the diffusion of cadmium ions.

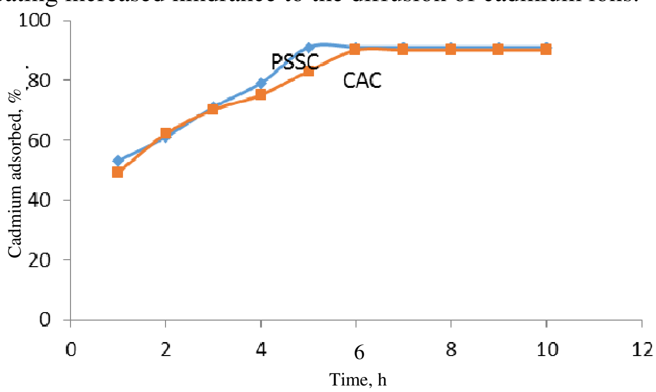

Figure 2. Effect of pH

Effect of carbon dosage

The effect of carbon dosage level on sorption of cadmium was carried out. Study was carried out by taking 10 ppm cadmium solution. Adsorbent dosage varied from 50 mg/L to 500 mg/L. 88% and 85% removal occurred at a dosage level of 250 mg/L and 300 mg/L for PSSC and CAC respectively (Figure 3). 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[8].

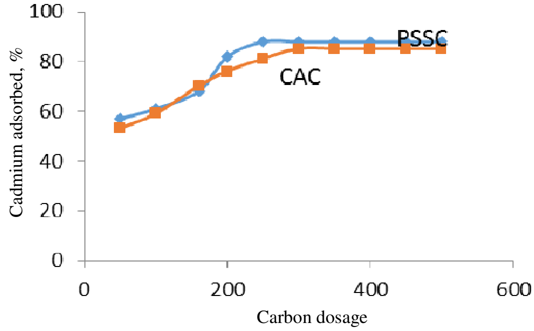

Figure 3. Effect of carbon dosage

Effect of particle size

Particles with small sizes have large surface areas and large adsorption capacities. It can be observed that the maximum adsorption efficiency of Cd(II) is achieved with PSSC and CAC particle sizes of <75 µm (Figure 4). 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[9].

Effect of agitation speed

An agitation speed of fewer than 160 rpm favors the optimal removal of metal ions by PSSC and CAC. The maximum removal of Cd(II) ions by PSSC and CAC occurred at 100 rpm. A high agitation speed may shift the equilibrium process of adsorption (Figure 5).

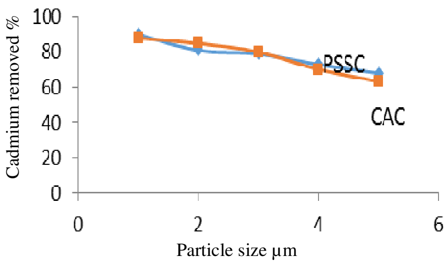

Figure 4. Effect of particle size

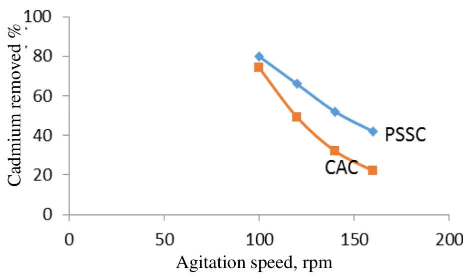

Figure 5. Effect of agitation speed

Effect of metal ion concentration

The batch experiment for metal ion concentrations was performed by varying cadmium concentrations. The concentrations varied from 5, 7.5, 10 ppm. The removal efficiency decreased with increase in concentration of cadmium, these may be due to unavailability of active sites of adsorbent with increase in metal ion concentrations (Figure 6).

Effect of temperature

The adsorption experiments were performed at five different temperatures *viz.,* 20, 30, 40, 50 and 60 ºC. At low temperatures, the mobility of metal ions in aqueous solution may be low; hence maximum amount of metal ions get removed especially at 30 ºC. At high temperatures, the thickness of the boundary layer decreases, due to the increased tendency of the metal ion to escape from the biosorbent surface to the solution phase, which results in a decrease in adsorption as temperature increases (Figure 7).

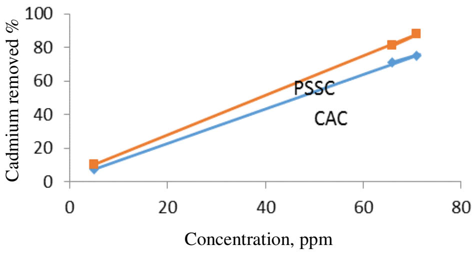

Figure 6. Effect of initial ion concentration

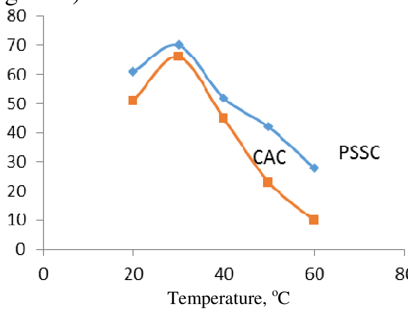

Figure 7. Effect of temperature

Freundlich adsorption isotherm

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

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

Where 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 indicates 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 adsorbents. The k values were found to be 0.3 and 0.6 for PSSC and CAC respectively, while 1/n is a function of the strength of adsorption in the adsorption process. If n=1 then the partition between the two phases is independent of the concentration. If the value of 1/n is below one it indicates a normal adsorption. On the other hand, a value of 1/n above one indicates cooperative adsorption.

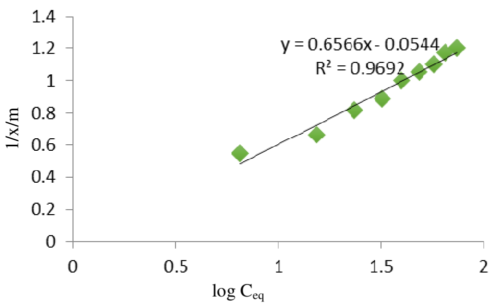

Figure 8. Freundlich adsorption isotherm for PSSC

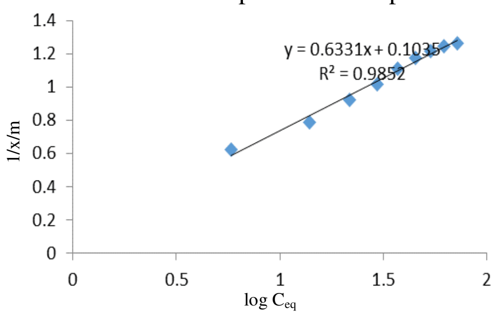

Figure 9. Freundlich adsorption isotherm for CAC

Langmuir adsorption isotherm

Langmuir isotherm 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 (Figures 10 & 11).

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

$$C_e=1/Q_ob+ C_e/Q_o \qquad (2)$$

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.* $1/C_{eq}$

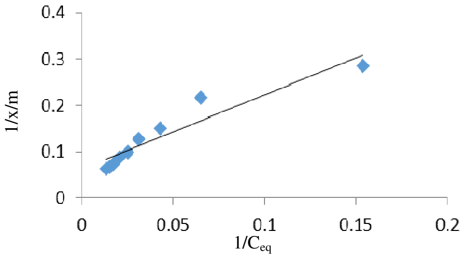

Figure 10. Langmuir adsorption isotherm for PSSC

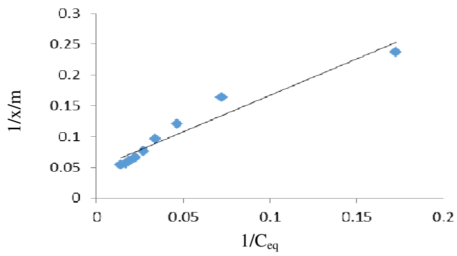

Figure 11. Langmuir adsorption isotherm for CAC

Temkin adsorption isotherm

The adsorbent- adsorbate interactions were studied by the Temkin isotherm. 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 (Figures 12 & 13). Its derivation is characterized by a uniform distribution of binding energies which was carried out by plotting the quantity adsorbed x/m against lnC_{eq}.

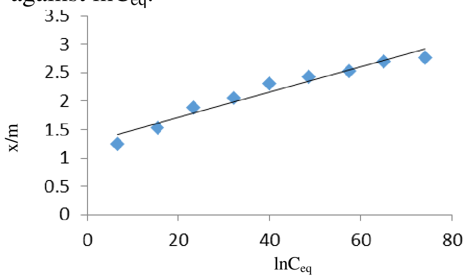

Figure 12. Temkin adsorption isotherm for PSSC

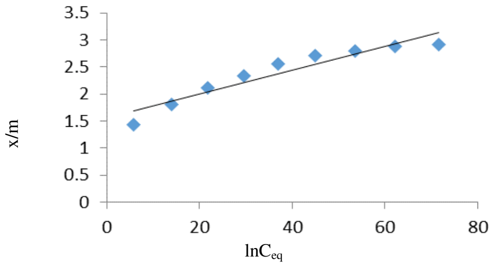

Figure 13. Temkin adsorption isotherm for CAC

Desorption studies

Desorption studies help to elucidate the nature of adsorption and to recover the precious metal from waste water using the adsorbent. Attempt was made to desorb the metal from spent carbons using HCl of various strengths. In highly acidic medium, protons (H^+ ions) displaces the Cd(II) by ion exchange mechanism. It was found that cadmium desorption increased with increased in the concentration of the acid. Concentration of 0.01N HCl was required to recover 87% PSSC and 78% CAC.

Instrumental analysis

The characterization of PSSC and CAC before and after adsorption using FT-IR, XRD confirmed the presence of Cd(II) ions onto the adsorbent.

Figures 14 &15 show the FT-IR spectrum of PSSC and CAC before and after adsorption. The frequency observed at 534.28 cm^{-1} is due to the presence of halo compounds and the frequency observed at 520.78 cm^{-1} is due to the presence of C-I stretching halo compound, alkyl halides after adsorption and it is a medium band. Figure 15 shows the presence of functional groups in CAC. The frequency observed at 673.10 cm^{-1} before adsorption is due to the presence C-Cl stretching and the frequency observed at 675.09 cm^{-1} may be due to alkyl halides or alkynes. The frequency observed at 597.80 cm^{-1} and 553.40 cm^{-1} before adsorption may be due to the presence of halo compounds and this frequencies shifted to 597.86 cm^{-1} and 555.50 cm^{-1} after adsorption may be due to the presence of stretching chloro or bromo alkenes.

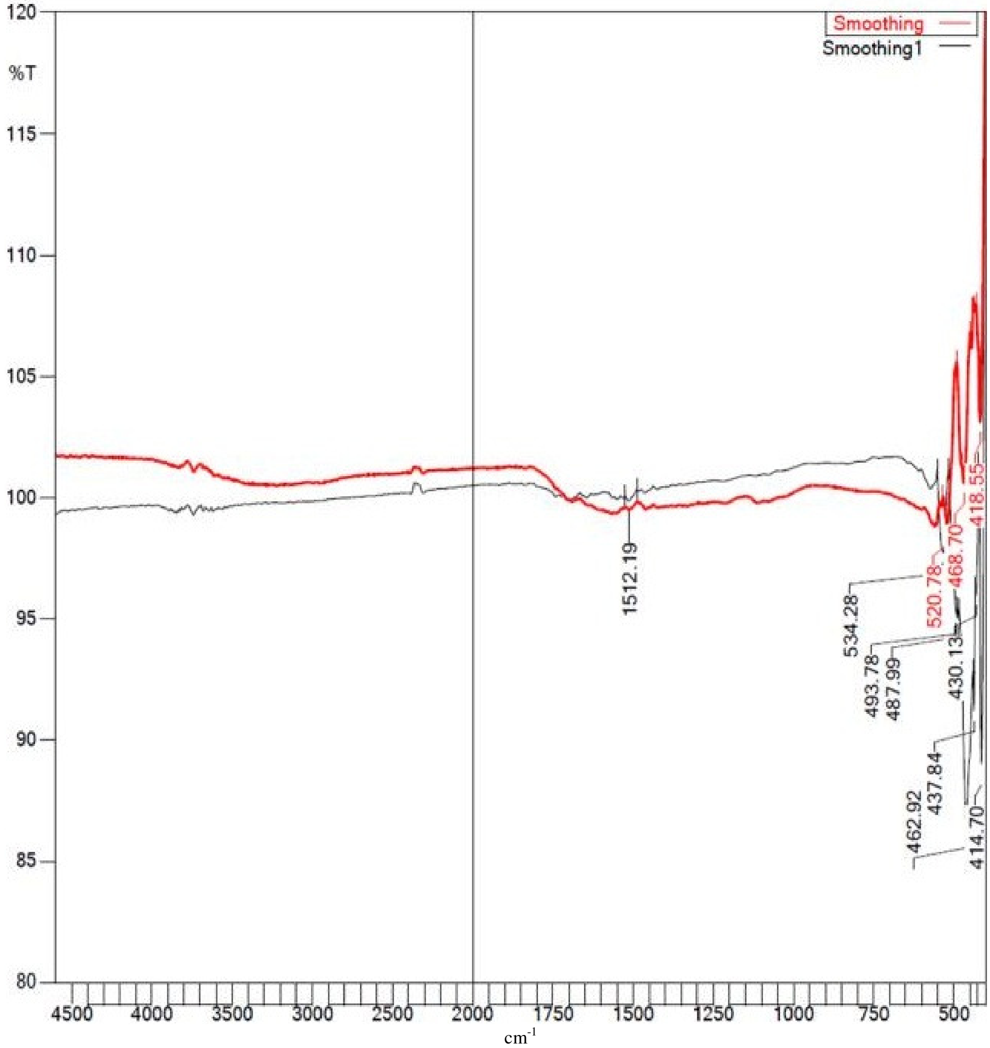

Figure 14. FTIR spectrum of PSSC before and after adsorption

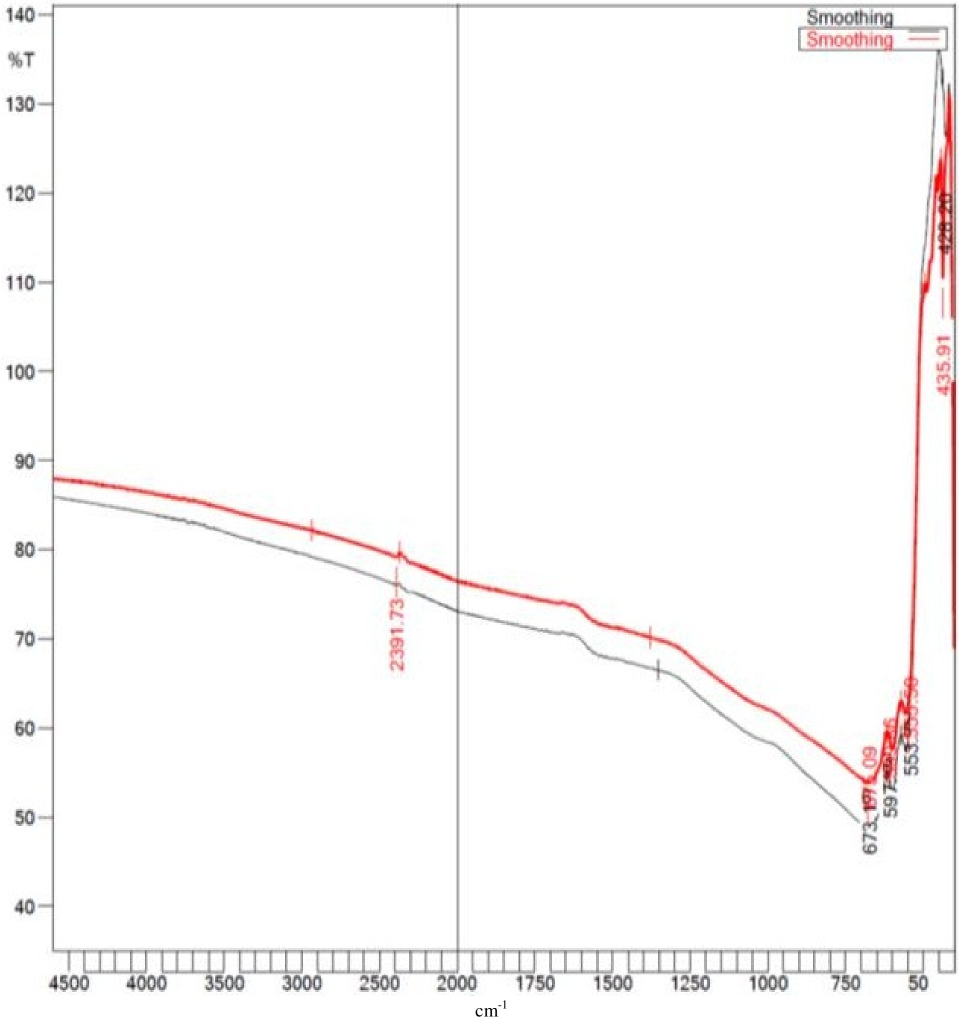

Figure 15. FTIR spectrum of CAC before and after adsorption

X-ray diffraction analysis before and after adsorption of PSSC and CAC

X-ray diffraction (XRD) analysis was used to identify the crystallographic structure of the samples. XRD analysis was carried out with a goniometer miniflex, 300/600 system.XRD analysis commonly measures crystalline and amorphous phases by sharp narrow diffraction peaks and broad hallow peaks. The XRD pattern for PSSC and CAC before and after adsorption of Cd(II) are shown in Figures 16(a-d). The pattern for Figures 16(a) and 16(c) for pure PSSC and CAC showed 2º theta peaks at 31.98º, 45.71º and for CAC at 26.56º, 44.0º. XRD pattern for Figure 16(b) for PSSC after adsorption the peaks diminished, this is attributed to the adsorption of metal ions onto the upper layer of the crystalline structure of the carbon surface by means of physisorption. XRD pattern Figure 16(d) for CAC after adsorption showed their peaks at 24.13º,43.14º. The sharp peaks present in the figure indicated that crystalline nature of material.

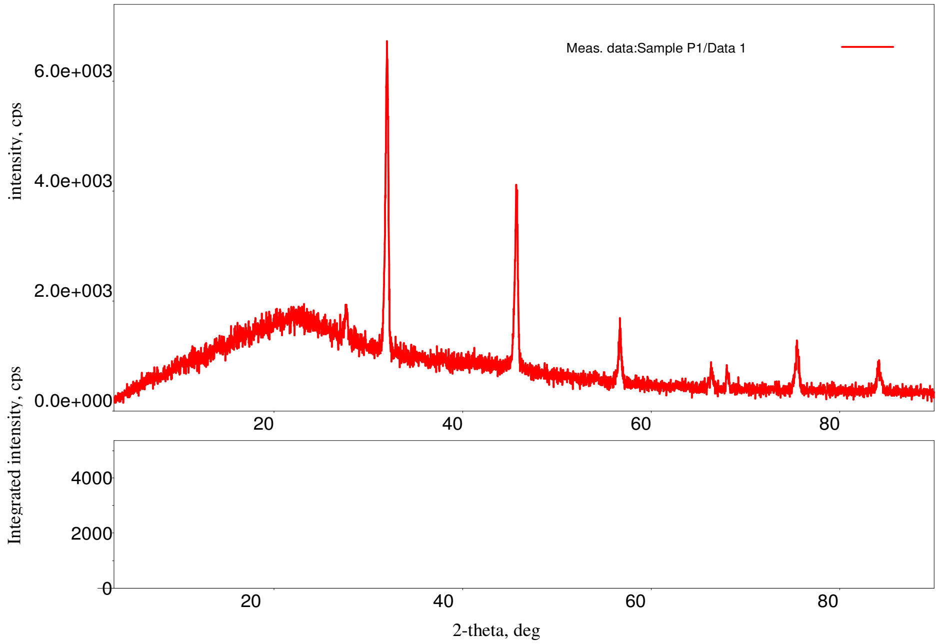

Figure 16(a). XRD pattern of PSSC before adsorption

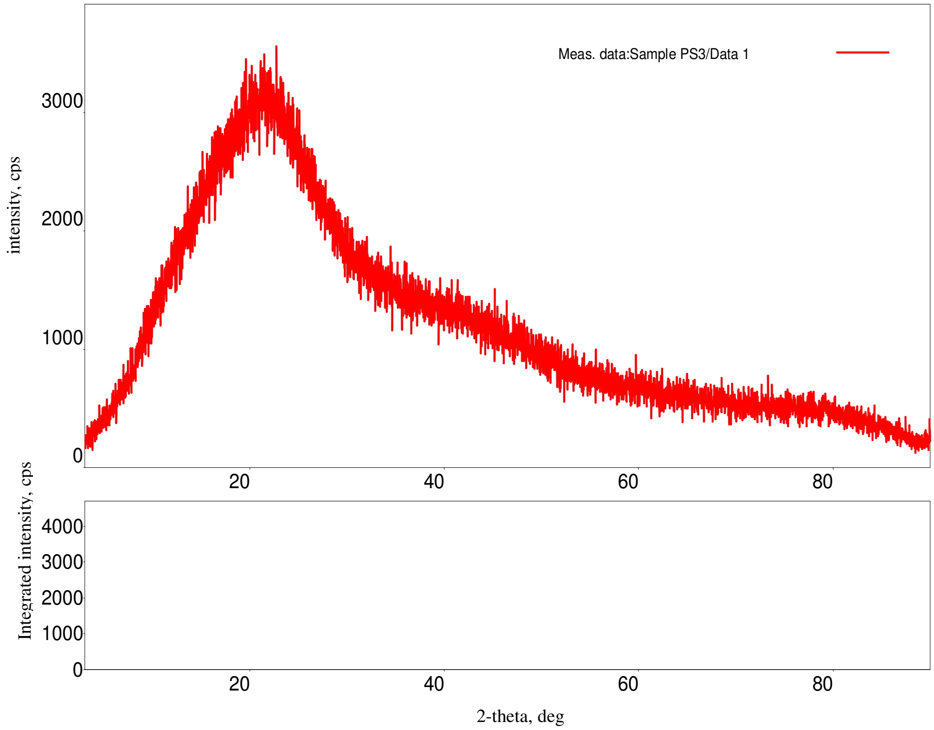

Figure 16(b). XRD pattern of PSSC after adsorption

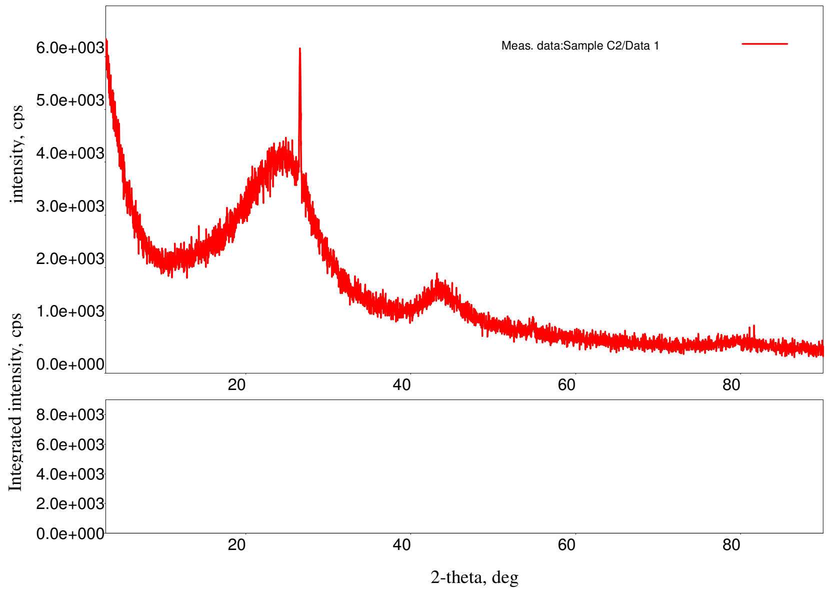

Figure 16(c). XRD pattern of CAC before adsorption

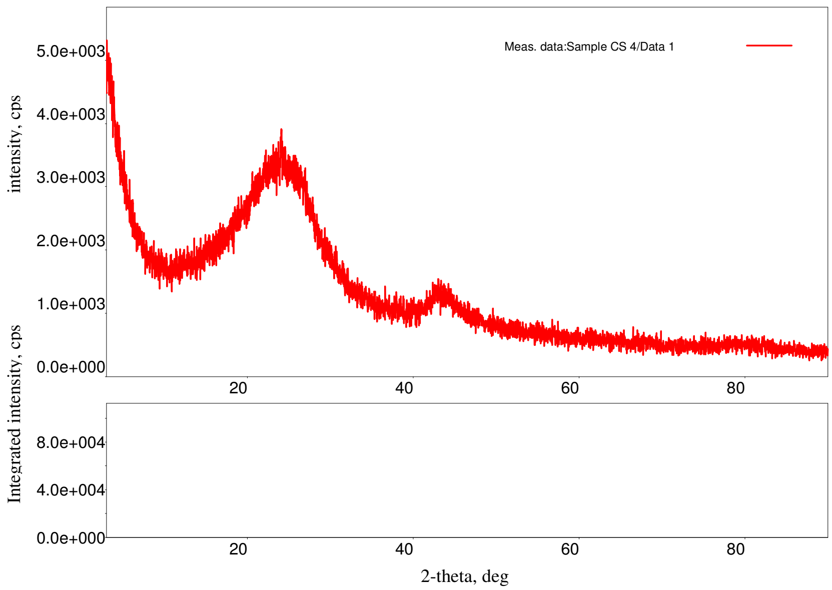

Figure 16(d). XRD pattern of CAC after adsorption

Conclusion

The experimental results indicated that pistachios seed shell and commercially activated carbon adsorbents can be successfully used for the adsorption of the Cd(II) ion from aqueous solutions. Experimental parameters such as contact time, pH, carbon dose, particle size, initial ion concentration, agitation speed, temperature must be optimally selected to obtain the highest removal of Cd(II) ion. The optimum equilibrium time were attained after 2 h for

PSSC and 4 h for CAC. The results indicated that pistachios seed shell adsorbent has higher adsorption capacity than commercially available carbon and optimum pH of 5.0 and 6.0 respectively for the adsorbents. Pistachio seed shell which is an agricultural waste material shows a highest removal efficiency than the CAC.

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