International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.11 No.03, pp 111-122, 2018

Adsorption of Cd(II) by Chemically Activated Pistachios Seed Shell and Commercially Activated Carbon from the aqueous solutions

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Abstract : In this investigation, the powder of pistachios seed shell carbon and commercially available carbon were used for the removal of Cd(II) from aqueous solutions. Pista seed shell carbon is a natural and eco friendly adsorbent. Pistachios seed shell carbon was prepared by charring with concentrated HCl and the carbon's characteristics such as moisture content, ash content, matter soluble in both water and acid, pH, decolourising power, iron content and ion exchange capacity were determined. The carbon is characterized by Scanning Electron Microscopy, Dispersive Energy of Spectroscopy (EDS), Fourier Transform-Infrared Spectroscopy (FT-IR) before and after adsorption. The experiments were performed in order to understand the kinetics of Cd (II) removal by PSSC and CAC. The results obtained indicate that PSSC is a very good adsorbent than CAC and it can be used for the separation of heavy metals from synthetic water.
Keywords : Adsorption, Pistachios seed shell, commercially available carbon, Isotherm, Desorption.

1, 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

DOI : http://dx.doi.org/10.20902/IJCTR.2018.110339

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 is used as an agricultural waste adsorbent and its removal capacity of Cd (II) from ground water is investigated.

2. Materials and methods:

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[7]:

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 110º C 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 0.2854g of $cdso_4$ (3 $cdso_4$. $8H_2O$) in water and diluted to 250 ml.

Batch Experiments:

Batch mode adsorption studies were carried out 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.

3, 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 available 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%, 15.2242% respectively. The decolourising power of PSSC was 210 mg/g whereas for CAC was 6 mg/g.

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

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. The increase in removal efficiency with contact time is due to increase in surface area and hence more active sites are available adsorption[8].

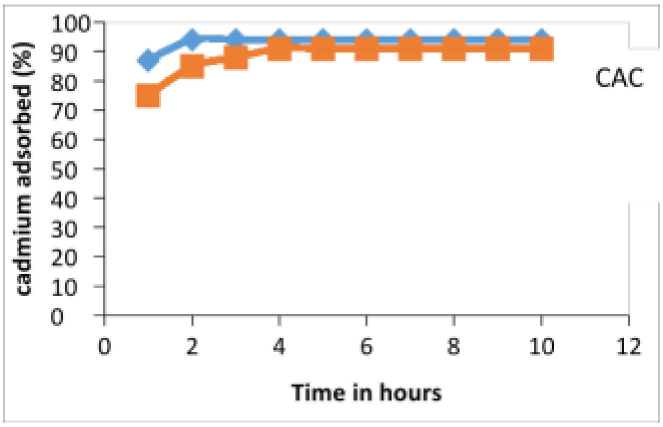

Fig .1Effect of Equilibrium time

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 pH6.0-10.00 for CAC. 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.

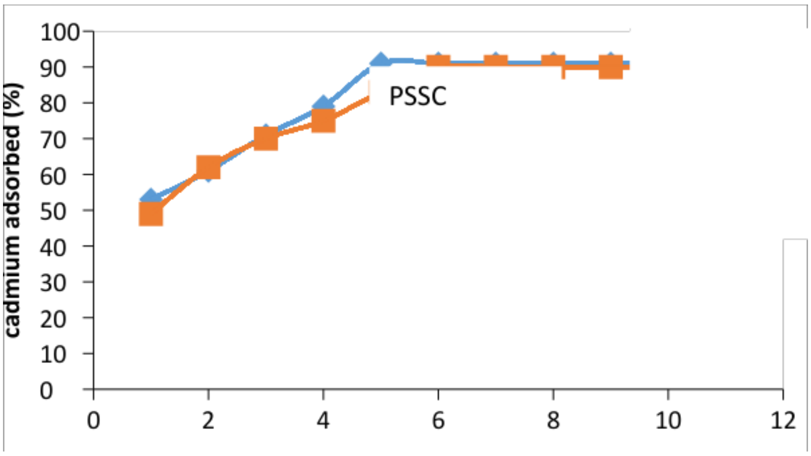

Fig .2 Effect of pH

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. 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[9].

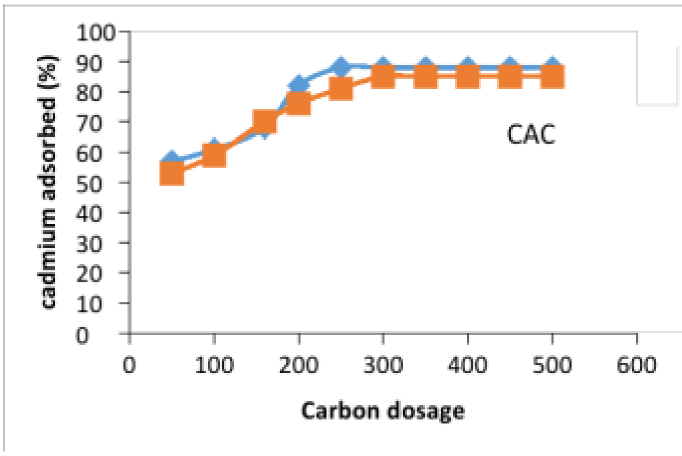

Fig 3 .Effect of carbon dosage

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 <75µm. 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[10].

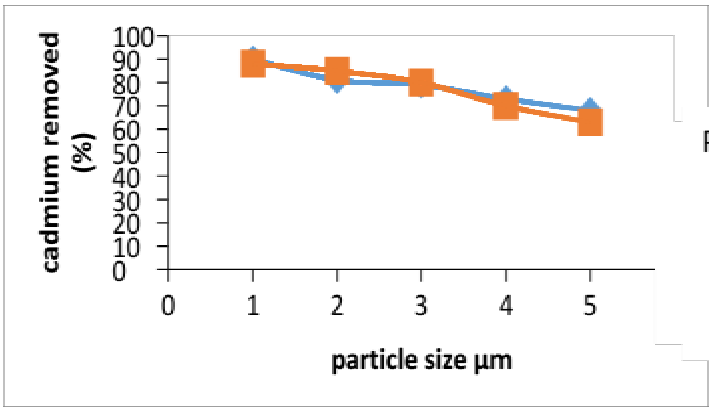

Fig .4 Effect of particle size

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.

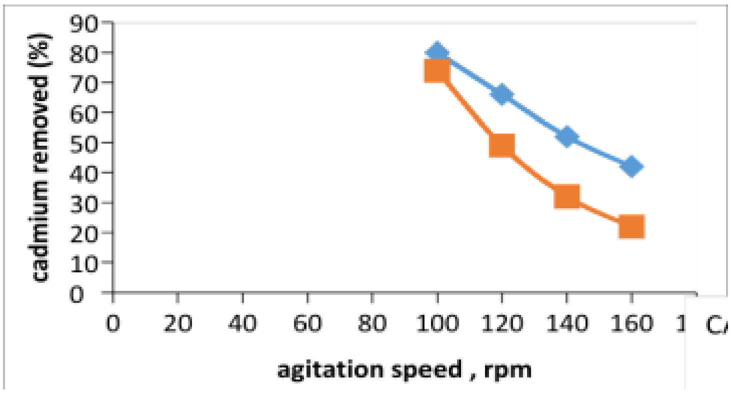

Fig .5 Effect of agitation speed

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.

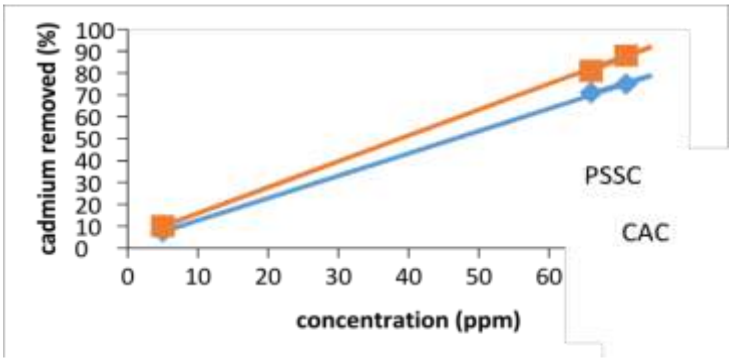

Fig .6 Effect of initial ion concentration

Effect of temperature:

The adsorption experiments were performed at five different temperatures *viz.*, 20, 30, 40, 50, 60ºC. At low temperatures, the mobility of metal ions in aqueous solution may be low; hence maximum amount of metal ions get removed especially at 30ºC. 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.

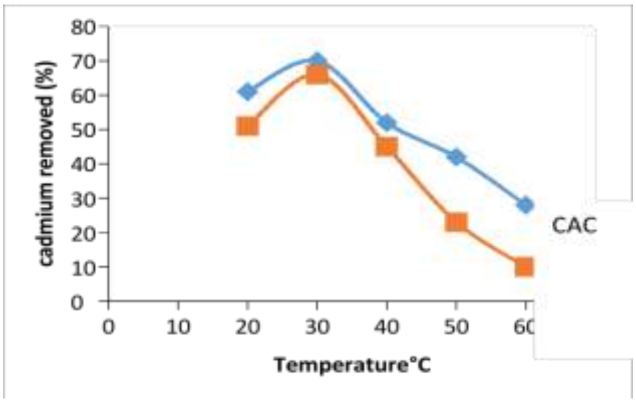

Fig 7 Effect of temperature

Adsorption Kinetics:

Kinetics:

Experiments were performed in order to understand the kinetics of Cd (II) removal by PSSC and CAC. The kinetics follows first order rate[114] expression given by Lagergren.

$\ln[1-u(t)] = -k't$

u(t) is the fractional attainment of equilibrium of Cd(II) and this was calculated by considering Cd(II) adsorption over the carbon range of 3-10ml/L were tried and shown in figures 20 and 21 respectively.

Kinetics of sorption describes the solute uptake rate, which in turn governs the residence time ofsorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of the cadmium removal was carried out to understand the behavior of this low cost carbon adsorbent. The adsorption of cadmium from an aqueous solution follows reversible first order kinetics, when a single species is considered on a heterogeneous surface.

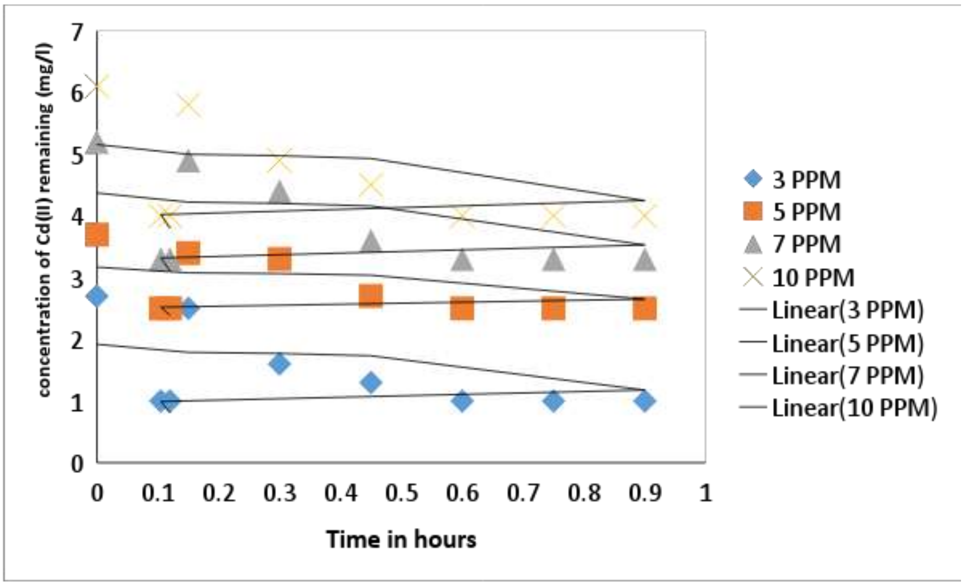

Fig 20 Kinetics sorption of PSSC

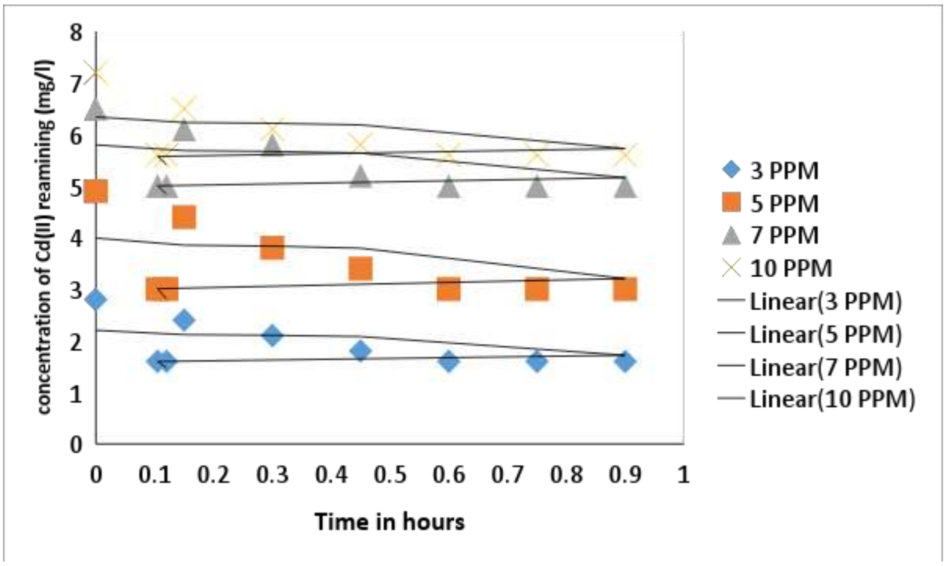

Fig 21Kinetics sorption of CAC

The u(t) values for different chosen time prior to equilibrium attainment were calculated for Cd ion for PSSC and CAC and the values are presented in the table . The ln[1-u(t)] values were plotted against the corresponding time for each concentration of Cd used in this study. Figures 22 and 23 represent the curves obtained for Cd with PSSC and CAC. The straight line nature of these curves for all concentration of Cd ion for PSSC and CAC indicated that sorption of Cd could be be approximated to first order reversible kinetics.

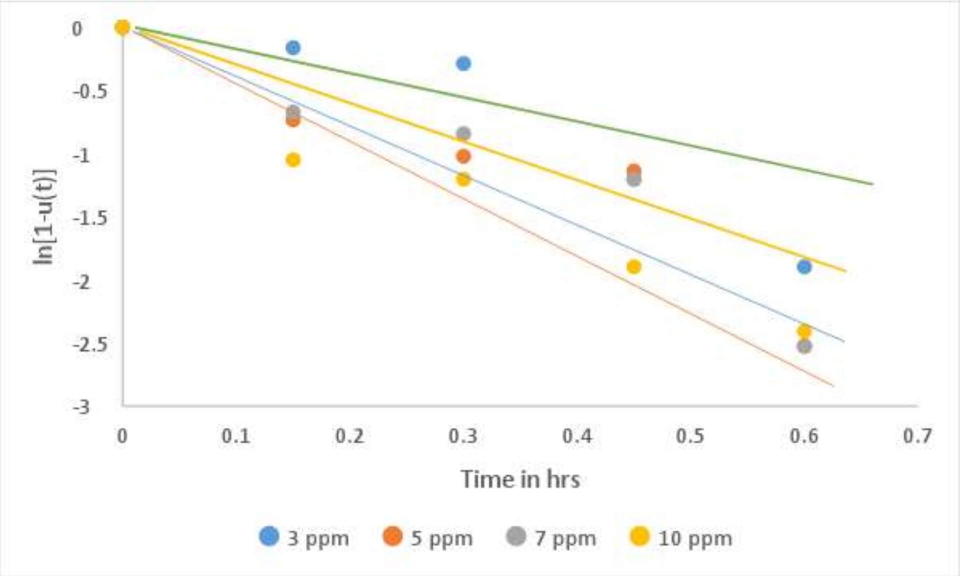

Fig 22 Lagergren pseudo first order kinetics for PSSC

The straight line nature of these curves for all concentration of Cd ion for PSSC and CAC indicate that sorption of Cd could be approximated to be first order kinetics.

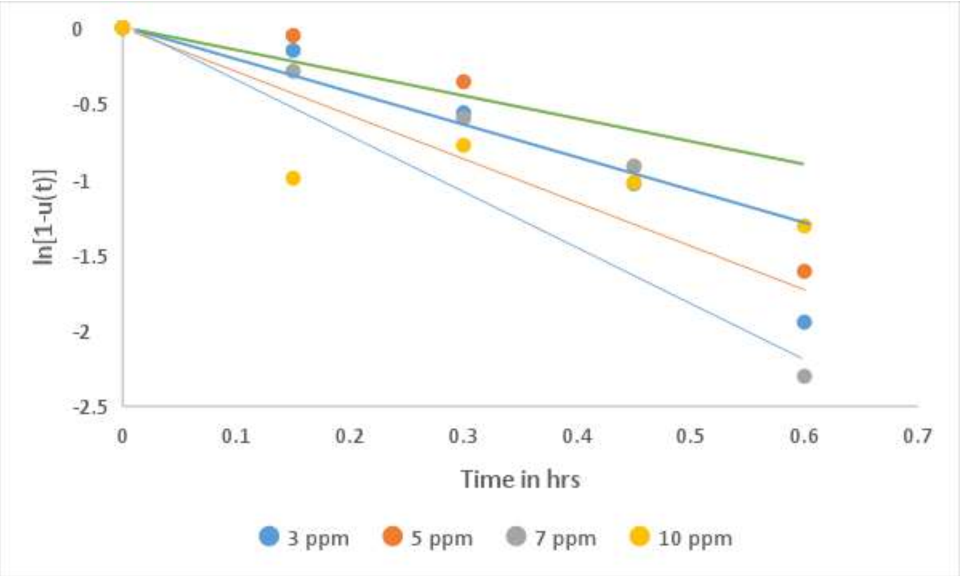

Fig 23 Lagergren pseudo first order kinetics for CAC

The pseudo first order plot showed reasonably good linearity till equilibrium time. This indicates that the adsorption follows first order kinetics and weak vander Waals'forces (physisorption). The correlation coefficient values show that the PSSC has high regression values than CAC.

4, 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.

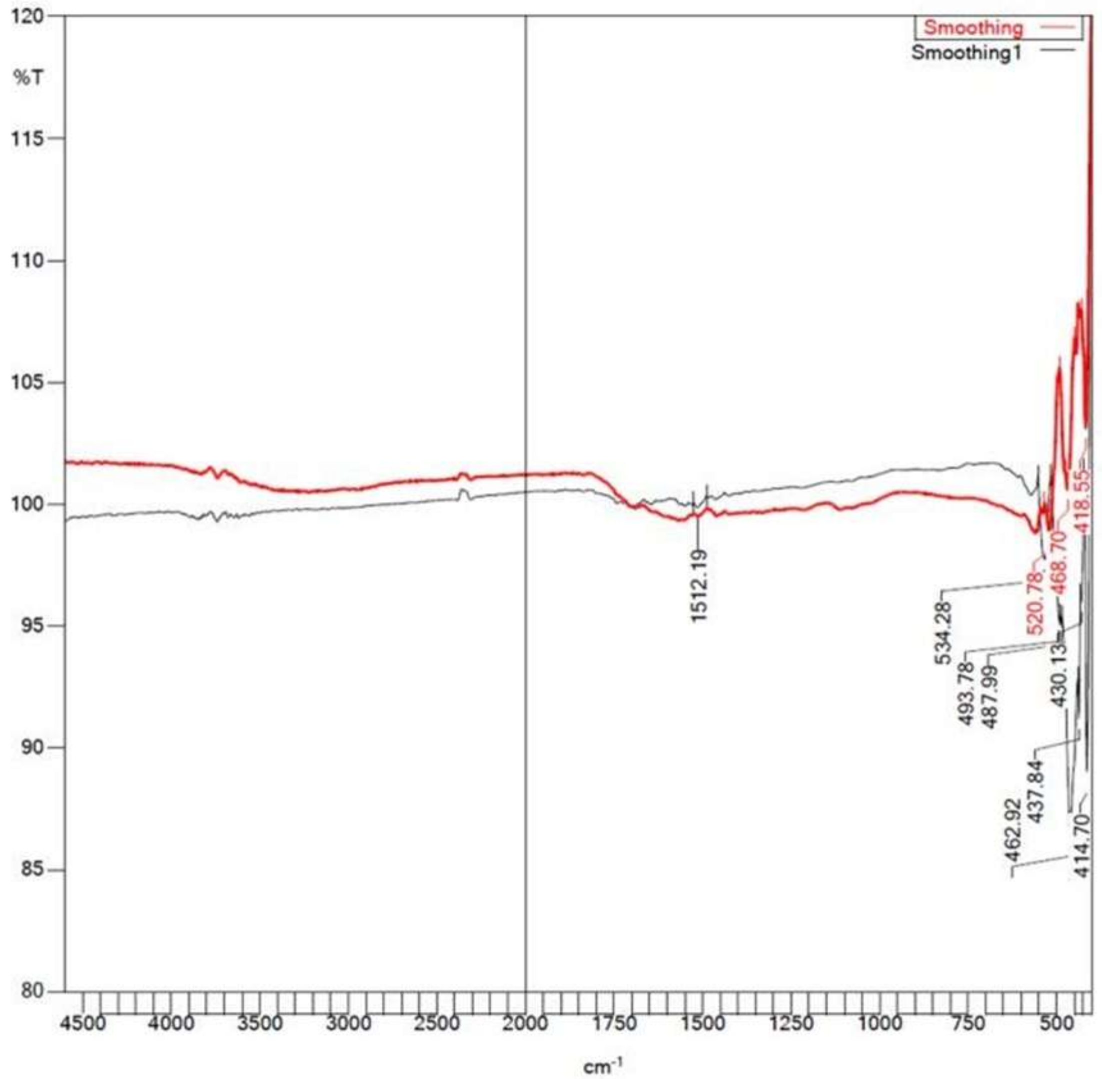

Fig 14 ,FTIR spectrum of PSSC before and after adsorption:

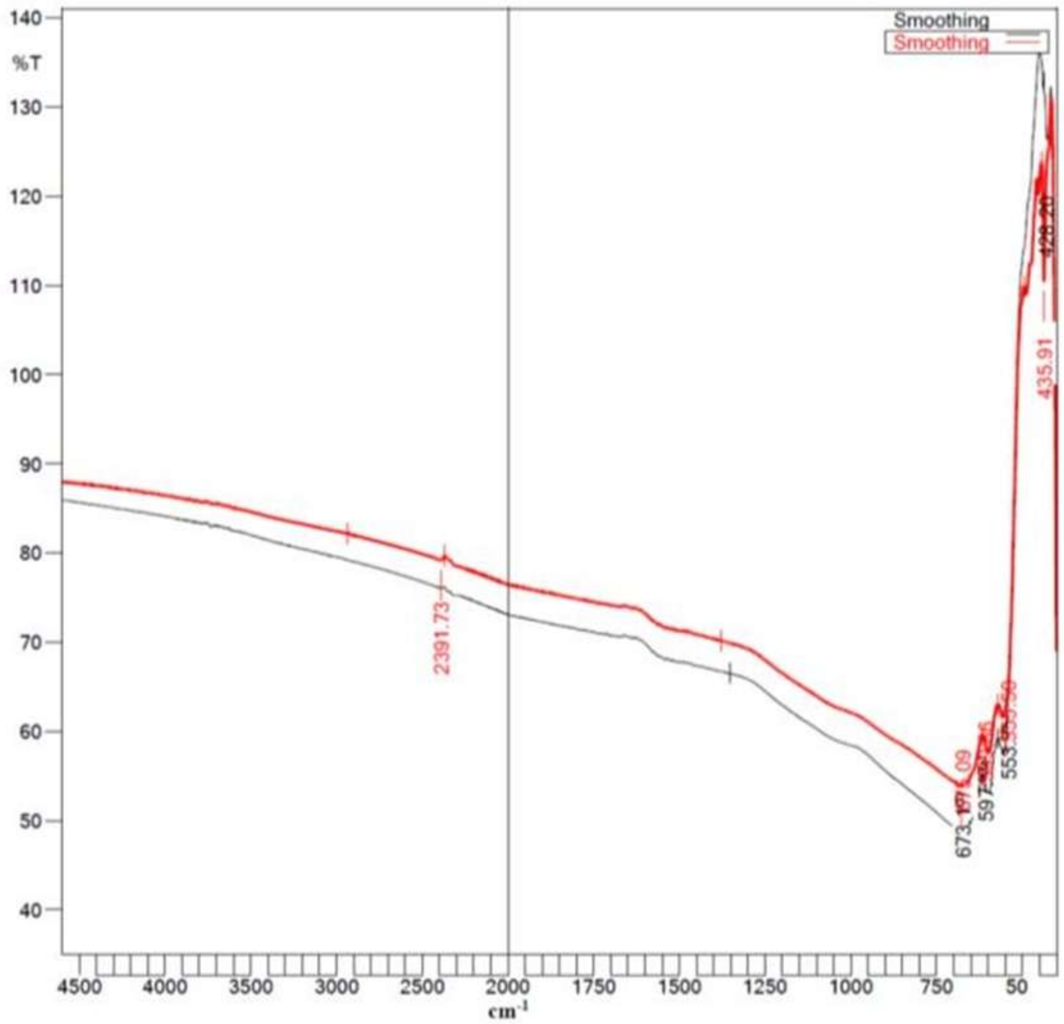

Fig 15, FTIR spectrum of CAC before and after adsorption

FIG (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. Fig 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.

Energy dispersive x-ray (EDX) analysis:

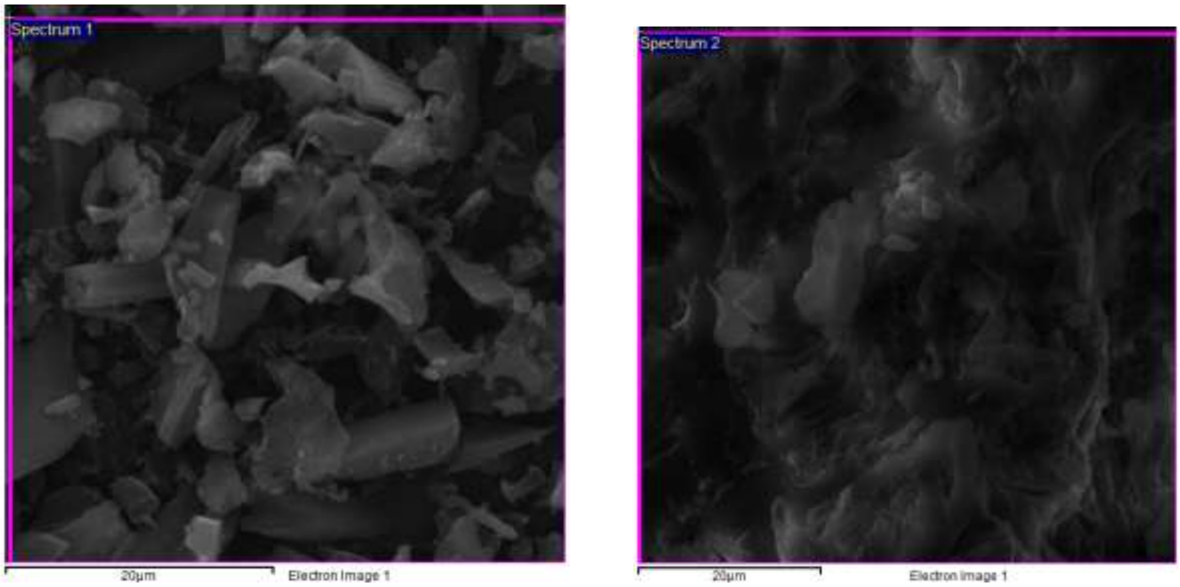

Fig 34 EDX image of PSSC before adsorption

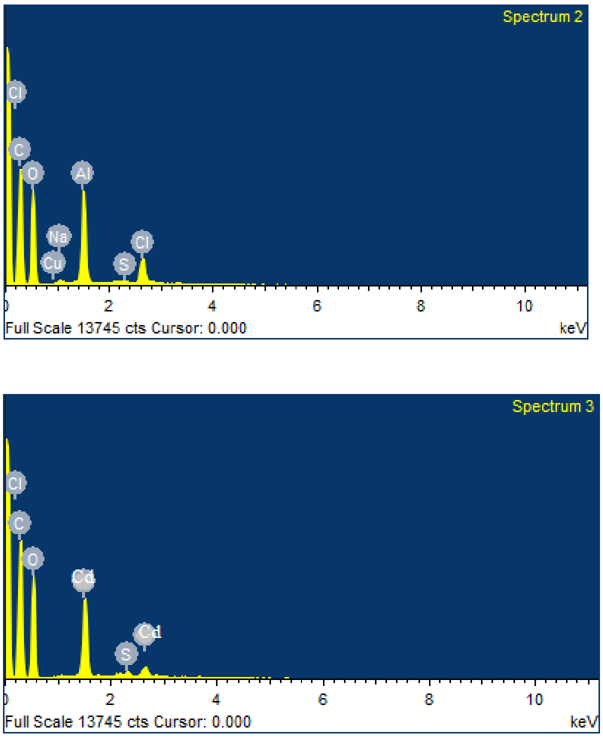

Fig 35 EDX image of PSSC before adsorption

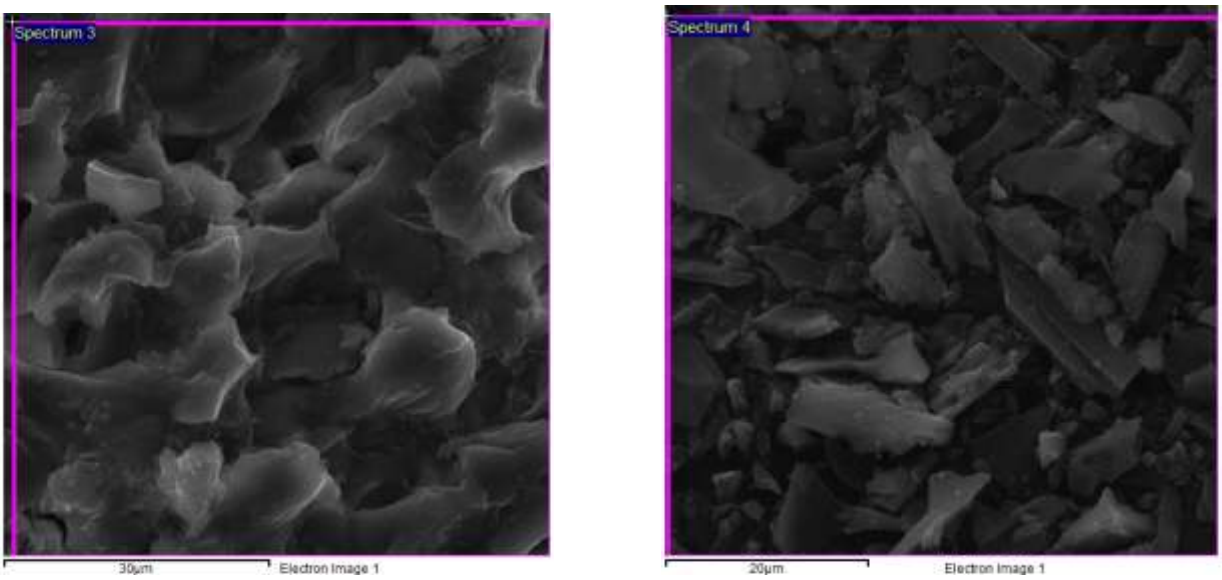

Fig 36 EDX image of CAC before adsorption

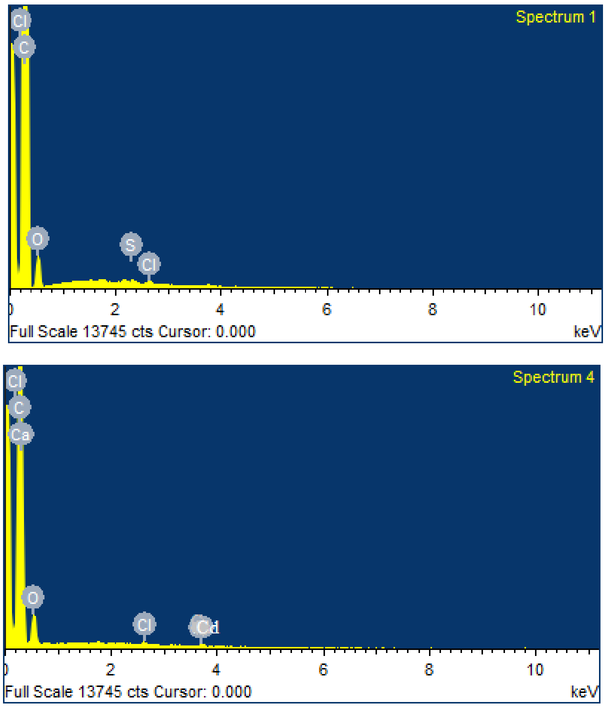

Fig 37 EDX image of CAC after adsorption

Figures 34, 35, 36 37 shows the typical EDX patterns for both the adsorbents PSSC and CAC before and after adsorption. The EDX pattern for the unloaded adsorbents did not display the characteristic signal of Cd, whereas for the Cd (II) loaded adsorbents ,a signal of the presence of Cd(II) was observed. Adsorption is confirmed by the presence of cadmium in the EDX spectrum of PSSC after adsorption shown in the figure35 . Carbon, oxygen, chlorine and their oxides were also present in the EDX spectrum which shows good adsorption capacity for PSSC.

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 2hrs for PSSC and 4 hrs 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 an highest removal efficiency than the CAC.

Acknowledgement:

We express our special thanks to the Head, Teaching and Non -teaching staff , Department of Chemistry for successful completion of this research work.

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