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RESEARCH ARTICLE

Studies on the Removal of Ni(II) from Aqueous Solutions Using Chemically Activated Pistachios Seed Shell and Commercially Available Carbon

M. S. MALAR SELVI*, S.AMALA FATIMA RANI and S. PAULINE SUGANTHI

Post Graduate and Research Department of Chemistry, Holy Cross College (Autonomous),
Tiruchirappalli-620 002, Tamilnadu, India
malarsampath@gmail.com

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Abstract: The powder of pistachios seed shell carbon (PSSC) and commercially available (CAC) carbon were used for the removal of Ni(II) from aqueous solutions. Pista seed shell carbon is a natural, low cost 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 adsorbents are tested by using batch experiments under controlled conditions. The effect of various experimental parameters such as equilibration time, pH, adsorbent dose are investigated. The obtained equilibrium adsorption data is fitted to the non-linear forms of Langmuir adsorption isotherm and Freundlich adsorption isotherm. 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 carbon, Langmuir isotherm, Freundlich isotherm

Introduction

Environment is a holistic view of the world as it functions at any time with a multitude of special elemental and socio-economic systems distinguished by quality and attributes of space and mode of behavior of biotic and abiotic forms[1]. The alteration in physical, chemical and biological characteristics of water may cause harmful effects on humans and aquatic life[2]. Toxic heavy metals are found naturally in the earth and become concentrated as a result of human caused activities[3]. The major source of nickel exposure is oral consumption as nickel is found in both food and water and may include human pollution, for example, nickel plated faucets contaminating water and soil, mining or smelting wastewater production, cooking with nickel-steel alloy housewares and eating in nickel-pigmented dishes. Other forms of exposure include breathing (polluted air from nickel metal refining, fossil fuel combustion and tobacco smoking) and skin contact (through direct contact with

Jewelry, shampoos, detergents and coins)[4]. Toxic heavy metals can bind to vital cellular components, such as structural proteins, enzymes and nucleic acids and interfere with their functioning[5]. Activated carbon, also called activated charcoal or activated coal, is a form of carbon processed to have small, low volume pores that increase the surface area available for adsorption or chemical reactions[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 work aims to prepare an activated carbon from pistachios seed shell (PSSC) by charring with concentrated HCl, characterize it and to compare its capacity with a commercial activated carbon (CAC) for the removal of nickel, a toxic heavy metal from wastewater by the method of adsorption.

Experimental

Pistachios seed shell were collected for sufficient quantity and treated with concentrated hydrochloric acid. The materials were 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, 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 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.

Characterization of PSSC and CAC

Physicochemical characterizations of carbon samples

Physicochemical characteristics such as, moisture content, ash content, apparent density, matter soluble in water and acid, pH, decolorising power, iron content, ion exchange capacity were determined using standard procedures[7]. The infrared spectrum was recorded in an Impart-420, Nicolet spectrometer.

SEM analysis

The morphologies and sizes of the samples were examined using Field Emission Scanning Electron Microscopy (FE-SEM) with an accelerating voltage 30 KV and filament current 20 kV and filament current of 20 mA for 45 seconds.

FT-IR spectral analysis

FT-IR spectra were recorded in a Perkin Elmer FT-IR spectrometer RSI in the region 4000-400 cm^{-1}

Isotherm procedure

Prior to isotherm studies, minimum contact times for adsorption equilibria to become established were estimated. Each experiment comprised three replicate 100 mL. Glass-stoppered bottles containing appropriate amount of adsorbent and 50 mL of adsorbate solutions of selected concentrations. Control flasks without the adsorbents were also prepared simultaneously. Mixtures were maintained in a rotary shaker at constant temperature (30, 45 or 60 ^{o}C). After the attainment of equilibrium the contents of each flask were filtered through Whatman no.41 filter paper, with the first 10 mL discarded. The filtered samples were then analyzed for unadsorbed metal ions. The equilibrium adsorption data were then fitted to Freundlich and Langmuir isotherm equations.

Freundlich $q_e= K_F C_e^{(1/n)}$ (1)

Langmuir $q_e= K_L C_e/(1+bC_e)=q_m bC_e/(1+bC_e)$ (2)

Where q_e is the adsorption capacity in mg/g; C_e is the equilibrium concentration of adsorbate (mg/L); K_F and n are Freundlich constants; K_L and b are Langmuir constants; q_m is the Langmuir monolayer adsorption capacity.

Effect of carbon dosage

10 mL of 10 ppm nickel sulphate solution and 10 mL of buffer solution of pH 3 were made upto 100 mL in 10 separate standard flasks. Various carbon dosages like 50 mg, 100 mg, 150 mg, 200 mg, 250 mg, 300 mg, 350 mg, 400 mg, 450 mg and 500 mg of PSSC and CAC were separately measured and transferred into different stoppered bottles. 100 mL of the nickel sulphate solution of pH adjusted to 3 were added to each bottle. The bottles were kept in an electric shaker for 3 hours to attain equilibrium. Then all the bottles were taken out allowed to stand for sometimes and filtered. First few mL of the filtrate were discarded from each bottle. Then 14 mL of the filtrate was pipette out into a 50 mL std. flasks. To this solution 20 mL of 0.5n HCl, 1 m mL of sodium citrate, 2 mL of iodine solution and 4 mL of DMG were added and the solutions were kept for 20 minutes. Then absorbance and percentage transmittance of each solution were noted using Spectroni-20 Spectrometer for the corresponding weight of carbon dosage.

Effect of equilibration time

An equal amount of 0.5 g of PSSC and CAC was transferred into 10 stoppered bottles. To each bottle 100 mL of 10 ppm solutions were added. Then all the bottles were kept in an electric shaker for adsorption. After one hour, one bottle was taken out from the shaker and allowed to stand for few minutes and filtered. First few mL of the filtrate were discarded. Then 14 mL of the filtrate were tandar out into a 50 mL standard flask. To this solution 20 mL of 0.5n HCL, 10 mL of sodium citrate, 2 mL of iodine solution and 4 mL of dimethylglyoxime were added and the solutions were made upto 50 mL usng the same filtrate and kept for 20 minutes. The instrument spectronic-20 spectrometrer was standardized using blank solutions. Then the absorbance and percentage transmittance of experimental solution was noted. The same procedure was repeated for all the bottles at the intervals of one hour.

Effect of pH

Different buffer solutions with pH 1-10 were prepared from the nickel sulphate solution (10 ppm). About 0.5 g of PSSC was tandardize into 10 stoppered bottles. To this 100 mL of each of this pH adjusted solutions were added and the bottles were kept in an electric shaker for 3 hours. The same procedure was carried with 0.5 g of CAC and the bottles were kept in the shaker for 4 hours. After 3 hours all the bottles containin PSSC were taken out, allowed to stand for few minutes and filtered. First few mL of the filtrate were discarded. Then 14 mL of the filtrate were pipette out into a 50 mL standard flask. To this solution 20 mL of 0.5 HCl, 10 mL of sodium citrate, 2 mL of iodine solution and 4 mL of DMG were added and the solutions were kept for 20 minutes. The instrument Spectronic- 20-spectrometer was tandardized initially using blank solution. Then the absorbance and the percentage transmittance of each solution were noted. After 4 hours, 10 bottles containing CAC were taken out from the shaker and using the above procedure[8], absorbance, percentage transmittance of each solution was noted.

Regeneration studies

100 mg of PSSC was weighed and transferred into 10 separate stopper bottles. To 100 mL of 10 ppm nickel solutions were added in bottles and kept in the electric shaker for 7 hours.

The bottles were taken out and allowed to stand for few minutes. The residue were washed with distilled water and taken in 10 stopper bottles. A series of 100 mL of 0.01N, 0.02N, 0.03N, 0.04N, 0.05N, 0.06N, 0.07N, 0.08N, 0.09N, 0.10N of HCl solutions were prepared. These solutions were transferred into the 10 stopper bottles and kept in the shaker for 3 hours. Then all the bottles were taken out and allowed to stand for few minutes and filtered. After filtration first few ml of filtrate were discarded from the bottle. Then 14 mL of the filtrate were pipette out into a 50 mL standard flask. Then 20 mL of 0.5N HCl, 10 mL sodium citrate, 2 mL iodine solution, 4 mL of DMG were added and the solutions were kept for 20 minutes. The instrument Spectronic-20 Spectrophotometer was standardized using blank solution. Then the absorbance and percent transmittance of each solution were noted. The above procedure[9] was repeated using 150 mg of CAC by keeping the equilibrium for 4 h.

Results and Discussion

Characterization of carbon samples

The parameters evaluated are given in Table 1.

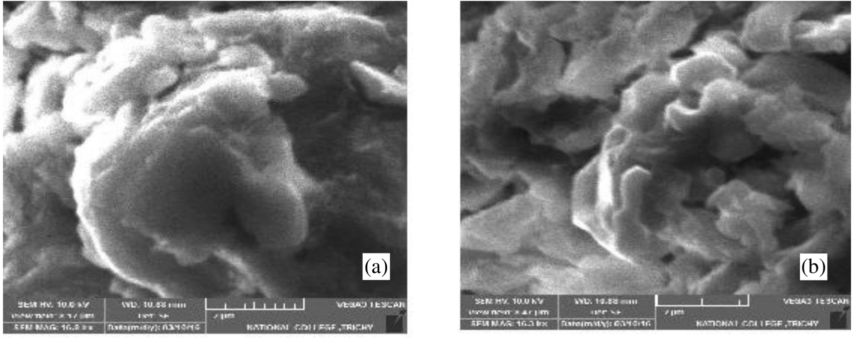
Table 1. Characterization data of carbon samples

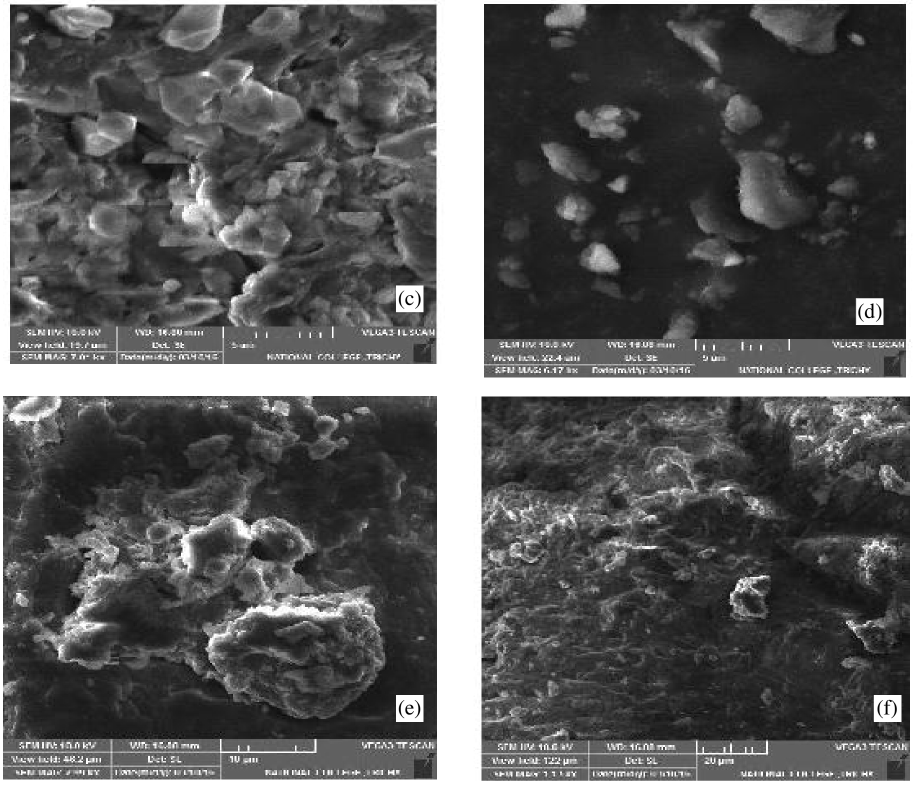
S.No	Characteristics	PSSC	CAC
1.	Moisture content, %	43.74%	7.869%
2.	Ash content, %	27.062%	4.2955%
3.	Apparent density, g/cc	0.7592 g/cc	0.1877g/cc
4.	Matter soluble in water, %	11.084%	15.2242%
5.	Matter soluble in acid, %	11.546%	9.5082%
6.	pH	4.75	7.93
7.	Decolourising power, mg/g	210 mg/g	6 mg/g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

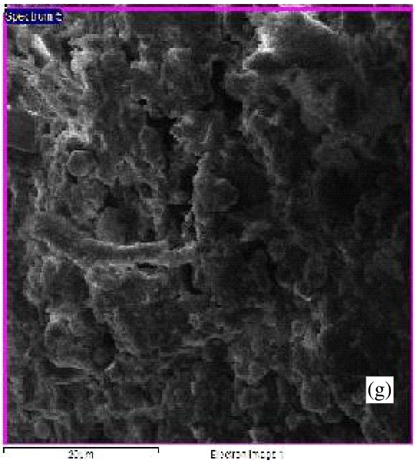
The process undertaken to study the characteristics reveal that PSSC seem to be better adsorbent compared to CAC. From the characteristics studies showed that suitability of acid treated Pistachios seed shell carbon seem to be higher quality than commercially activated carbon for the removal of nickel ions.

SEM analysis

Figure 1 shows the SEM images of Pistachios seed shell carbon before adsorption. All the SEM images of PSSC indicates high surface roughness and irregularity. The SEM images also indicate many pores are present in the surface of the absorbent. This pores indicate the surface area is more, which lead to the better adsorption of PSSC, during the adsorption process.







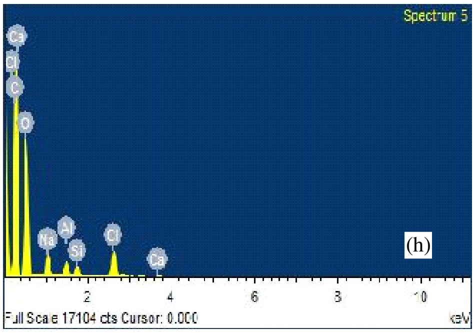


Figure 1(a-f). SEM images of Pistachios seed shell carbon before adsorption;
Figure 1(g). EDS image of PSSC before adsorption
Figure 1(h). SEM images of PSSC before adsorption

The image indicates the existence of the elements such as carbon, oxygen, sodium, aluminium, silica, chloride and calcium. Aluminium, silica, calcium and their oxides generally shows high adsorption capacity. This may be the reason for the good adsorption of PSSC.

FT-IR spectra of activated carbons

Figure 2(a,b) show the FT-IR spectrum of CAC and PSSC before and after adsorption. The intense band of this figure clearly explains the high adsorption capacity of PSSC and CAC. Figure 2(a) show the presence of many functional group in PSSC. The frequency observed at 1508.33 cm^{-1} is due to the presence of nitro compounds N-O Asymmetric stretching and the frequency observed at 1327.03 cm^{-1} is due to the presence of N-O Symmetric stretching. The frequency observed at 1217.08 cm^{-1} and 2922.16 cm^{-1} may be due to the C-O stretching and C-H stretching respectively. Figure 2(b) shows the presence of many functional groups in CAC. The frequency observed at 1431.18 cm^{-1} is due to the presence of carboxylic acid O-H bending and the frequency observed at 1163.08 cm^{-1} is due to the presence of aliphatic amines C-N stretching. The frequency observed at 1089.78 cm^{-1} is due to the presence of esters C-O stretching and aliphatic amines C-N stretching. The frequency observed at 792.74 cm^{-1} is due to the presence of aromatic C-H out of plane. Figure 2(a,b) 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.

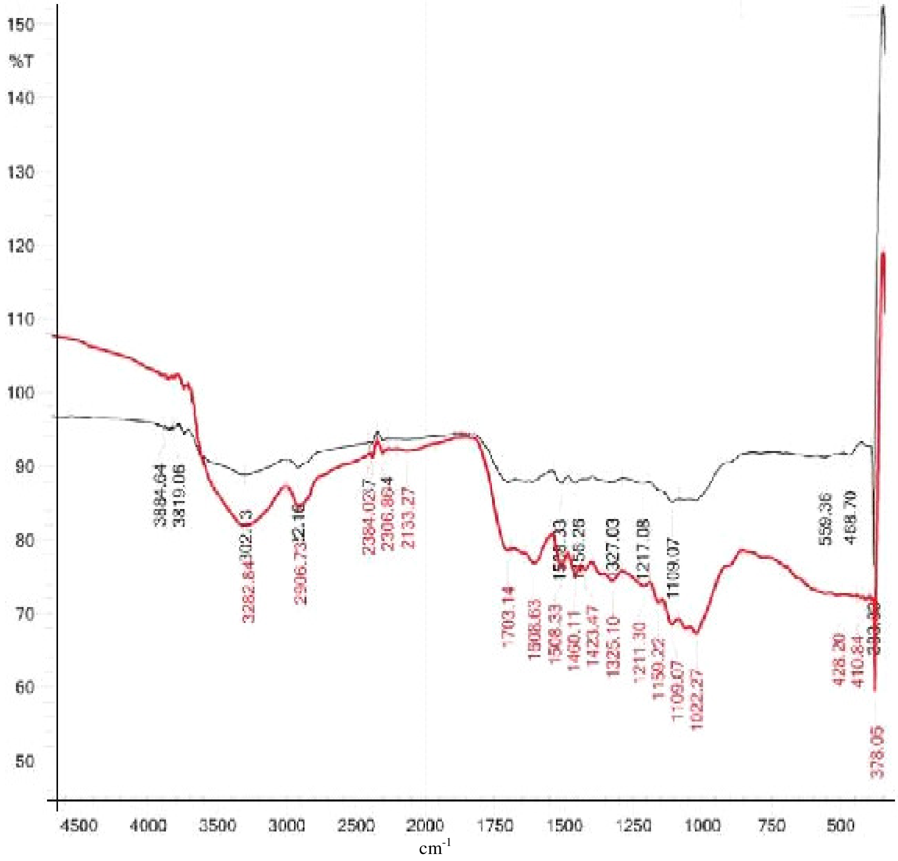


Figure 2(a). FT IR spectrum of PSSC before and after adsorption

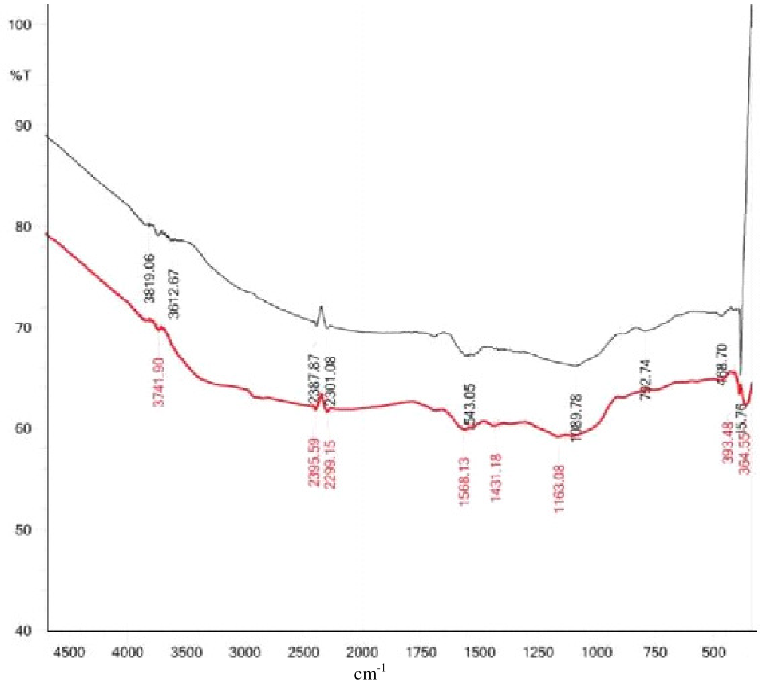


Figure 2(b). FT-IR spectrum of CAC before and after adsorption

Isotherm analysis

The assumption associates with the Langmuir isotherm are well known[10]. Adsorption cannot proceed beyond monolayer coverage and all adsorption sites are equivalent. The Freundlich model, on the other hand, assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. For each and every individual adsorption system, the data were fitted to the two isotherm equations Figure 3 & 4. All the curves were under Giles classification[11].

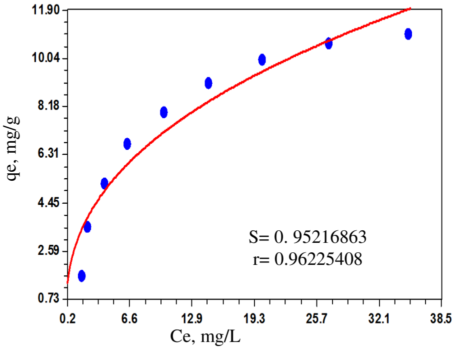


Figure 3. Freundlich isotherm fit to the adsorption of Ni(II) on PSSC at 30 °C (*Conditions: adsorbent dose 0.5 g/100 mL of adsorbate solution; initial concentration of metal ion solutions, Ci = 10-90 mg/L for Ni*)

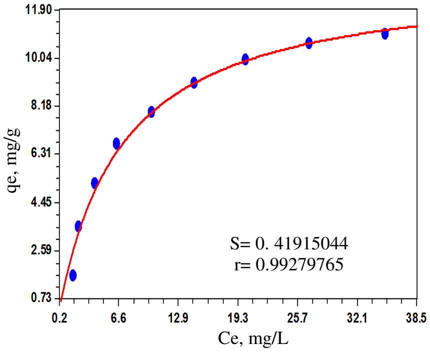


Figure 4. Langmuir isotherm fit to the adsorption of Ni(II) on PSSC at 30 °C

According to Treybal[12] it has been shown using mathematical equations that n values between 0 and 1 represent beneficial adsorption. Indeed, the n values found for all the adsorption systems fall in this range. The Langmuir constant b is a measure of adsorption intensity and the parameter q_m is measure of adsorption capacity. Adsorption capacity of the adsorbents towards metal ion decrease, whereas the adsorption intensity decreases in the opposite order. The b values found indicate stronger interaction forces between carbon surface and Ni(II) ions. The b values determined are further used to calculate the dimensionless separation factor, R_L[13,14], defined as

$$R_L = 1/(1+bC_i) \tag{3}$$

Where C_i is the initial solute concentration. The magnitude of R_L value gives an idea about the nature of adsorption equilibrium: the process is non-spontaneous when R_L is greater than one; favourable when R_L lies between 0 and 1 and irreversible when R_L is zero. In all the systems studied, R_L values were comprised between 0 and 1 indicating favourable adsorption of all the metal ion on the activated carbon.

Kinetics

To describe the adsorption kinetics a pseudo-second order rate model reported in the literature was applied[15-17] in the following form

$$t/q_t = (1/h) + (1/q_{e(2)})t \tag{4}$$

Where, h is the initial sorption rate (mg g^{-1} min^{-1}); $q_{e(2)}$ is the amount of metal ion adsorbed at equilibrium (mg/g) and q_t is the adsorbed at time t (mg/g).

The second order kinetic parameters evaluated are presented in Figure 5. Good agreement between the predicted and experimental results was found. Hence the applied pseudo-second order rate model succeeded in representing properly the experimental data for the adsorption of metal ions with high correlation coefficients (r^2> 0.99). It is also to be noted that the experimental adsorption capacities ($q_{e(exp)}$) are very close to the adsorption capacities predicted by the second order kinetic model ($q_{e(2)}$), these values are also furnished in Figure 5.

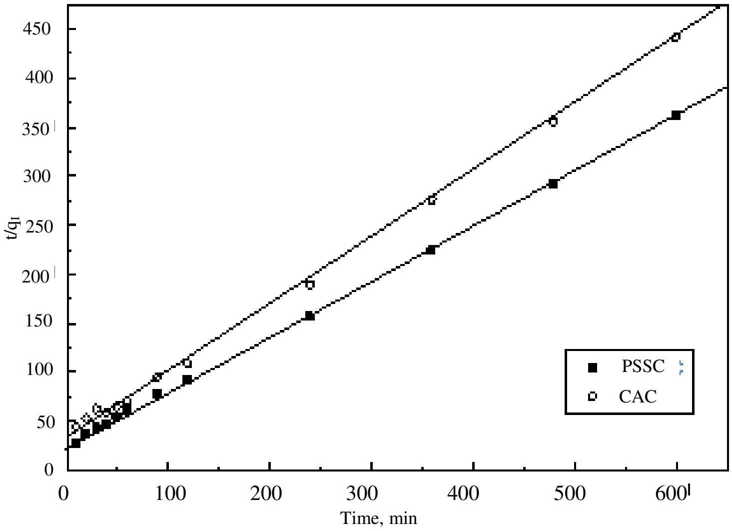


Figure 5. Second order Kinetic Plots (Ni^{2+})

Thermodynamic studies

Thermodynamic parameters such as Gibb's free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated using the following expressions:

$$K_C = \frac{C_{ae}}{C_e} \tag{5}$$

$$\Delta G = -RT \ln K_c \tag{6}$$

$$\log K_C = \left[\frac{[\Delta S]}{2.303R}\right] - \left[\frac{\Delta H}{2.303RT}\right] \tag{7}$$

Where K_c is the equilibrium constant for the distribution of metal ion between the liquid and solid phases; C_{ae} is the solid phase metel ion concentration, mg/L; C_e is the liquid phase metal ion concentration, mg/L; T is absolute temperature, K and R the gas constant. Equation 7 was used to construct Van't Hoff plots and ΔH and ΔS were calculated from the slope and intercept of the Van't Hoff plot, respectively. Thermodynamic parameters evaluated for varied metal ion concentrations are listed in Table 2.

Table 2. Thermodynamic parameters for the adsorption of metal ion on PSSC

Metal ion	C_i mg/L	ΔG, kJ mol^{-1}			ΔH	ΔS
		30 °C	45 °C	60 °C	kJ mol^{-1}	J/K mol^{-1}
Ni(II)	10	-3995.14	-4159.37	-4532.19	5922.211	32.60758
	20	-5178.98	-5439.62	-5753.46	56075075	38.02622
	30	-4708.93	-4826.98	-5435.1	70254203	41.5493
	40	-4187.45	-4316.56	-4745.38	54083295	33.89044
	50	-3458.4	-3534.04	-4078.18	59873056	33.56494
	60	-2837.97	-3116.14	-3391.76	54150765	29.62063
	70	-2277.02	-2428.07	-2701.31	41288270	22.89998
	80	-1702.17	-2079.59	-2305.15	59180979	27.83994
	90	-1119.99	-1272.75	-1562.19	43026901	19.72156

The ΔG values obtained for most PSSC-metal ion system were positive indicating that PSSC is less effective in removing metal ion from aqueous solutions. The positive values of ΔH obtained for all the processes are further conformations that they are endothermic, which is an indication of strong interaction between the adsorbate and the adsorbent. The positive values of ΔS suggest increased randomness at the solid-liquid interface during the adsorption of metal ion. The adsorbed solvent (water) molecules, which are displaced by the adsorbated species, gain more translational entropy than is lost by the adsorbate ion. Furthermore, before the adsorption process takes place the adsorbate ion is heavily solvated and this order is lost when the ions is adsorbed on the surface, due to the release of solvated water molecules.

Effect of carbon dosage

A graph was plotted using percentage of nickel absorbed against carbon dosage of the solution for both the absorbents. The maximum adsorption took place at the particular carbon dosage that was considered as the maximum dosage for both the adsorbents.

Figure 6 clearly reveals that the carbon dosage used for removal of Nickel using PSSC and CAC which represents the removal of Nickel as a function of carbon dosage by PSSC and CAC respectively it shows that for quantitative removal of Nickel from 100 mL of solutions containing mg/L. Nickel is a minimum dose of 100 mg of PSSC was required, but for CAC is a minimum dose of 150 mg was required.

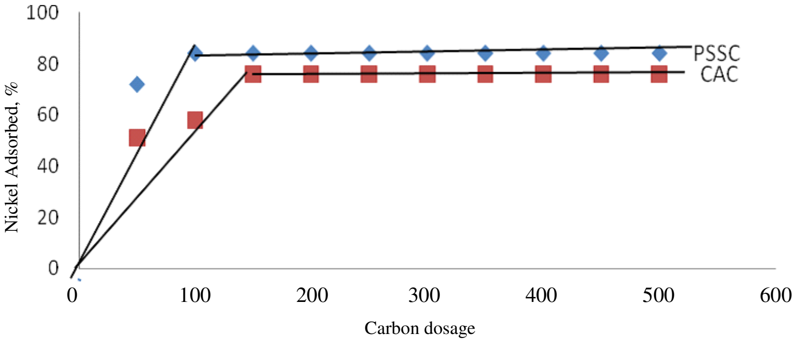


Figure 6. Effect of carbon dosage

Effect of contact time

A graph was plotted using percentage of Ni(II) adsorbed *versus* time at which the maximum adsorption took place were considered as the equilibration time.

Figure 7 shows the effect of equilibrium time on the removal os Ni(II) by PSSC and CAC. The removal increases with increase in time and attains equilibrium at third and fourth hour for PSSC and CAC respectively. This indicates the residence time required for maximum removal of Nikel by PSSC was less than that for CAC by one hour. The percentage of removal for PSSC is found to be 87 and 82 for CAC.

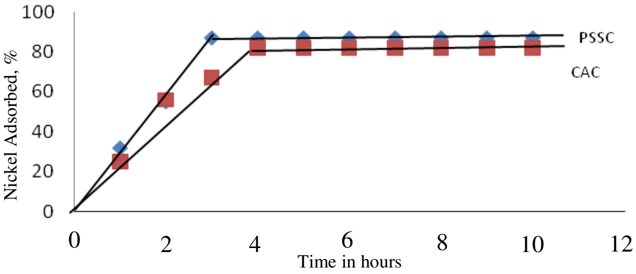


Figure 7. Effect of contact time

Effect of pH

A graph was plotted by using percentage of nickel absorbed against pH of the solution for both absorbents. The maximum adsorption took place at particular pH that was considered as the result of the selected pH for both the adsorbents at which maximum adsorption takes place.

Figure 8 show the effect of pH on the removal of nickel by PSSC and by CAC with increase in pH, the percentage removal increase and reach the maximum at pH 3. The percentage of nickel removal by PSSC is higher by 78% than that of CAC 73%. The influence of pH on the removal of nickel 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 Ni(II) is more favorable.

Effect of temperature

The equilibrium studies for all the systems were conducted at two more temperatures in addition to room temperature (30 °C), namely 45 and 60 °C. For all the systems increase in temperature resulted in greater adsorption. Figure 9 and 10 show the effect of temperature for the Ni(II)-PSSC system and Ni(II)-CAC system.

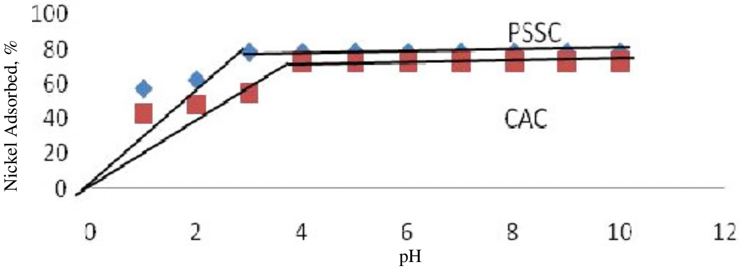


Figure 8. Effect of pH

The increased adsorption at higher temperatures can be due to one or more of the following reasons. Acceleration of some originally slow step(s)[18]; creation of some new activation sites on the adsorbent surface[18] and decrease in the size of the adsorbing species[19]. This could well occur due to progressive desolvation of the adsorbing ion as the solution temperature increases.

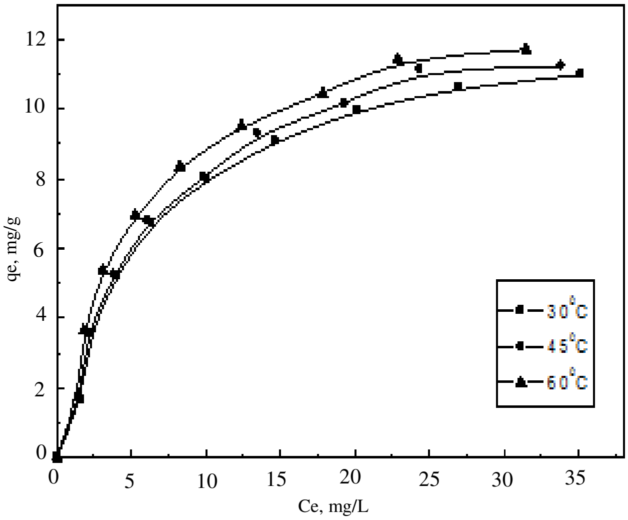


Figure 9. Effect of temperature: Adsorption of Ni(II) –PSSC

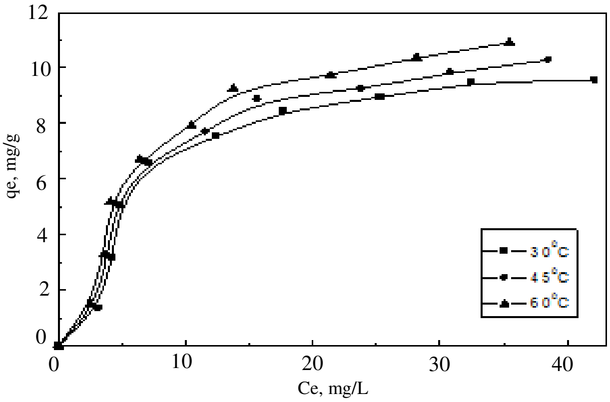


Figure 10. Effect of temperature: Adsorption of Ni(II) –CAC

Regeneration studies

Regeneration studies help to elucidate the adsorption nature and help to recover metals from water and adsorbent (Table 3). 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 73% of CAC respectively.

Table 3. Regeneration studies

Concentration of HCl, N	Percentage of nickel regenerated, %	
	PSSC	CAC
0.01	77	73
0.02	73	70
0.03	67	68
0.04	65	61
0.05	58	55
0.06	48	50
0.07	40	45
0.08	34	40
0.09	28	37
0.10	23	25

Conclusion

Investigation from the above studies using the adsorbents as PSSC and CAC, the following conclusions were drawn, since the preparation of PSSC was much easier and pista seeds are abundantly available as 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 and other 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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