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Sequestering Potential of Peach Nut Shells as an Efficient Sorbent for Some Toxic Metal Ions from Aqueous Media: A Kinetic and Thermodynamic Study

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Abstract

The peach nut shells (PNS) potential as a low cost biosorbent for separation of certain metal ions from aqueous media was investigated. The effects of different parameters such as pH, shaking speed, initial metal ions concentration and their contact time with adsorbent on sorption efficiency of biosorbent was investigated to optimize the parameters for maximum sorption. The biosorbent was characterized by FT-IR spectroscopy and a significant increase in sorption was noted with rise in pH of metal ions solution and maximum sorption was observed at pH 6. The isothermal data was fitted to Langmuir, Dubinin–Radushkevich (D–R) and Freundlich isotherms. The equilibrium process was best fitted to Langmuir isotherm. The removal efficiency of chemically activated samples was found to be ~35 to 45% greater than raw sample. These results showed that peach nut shell was an effective biosorbent for remediation of contaminated water with lead (II), Nickle (II) and Chromium (III) ions. Being low cost material, PNS has a potential to be exploited in waste water treatment technologies. This study shows that even at very low concentration of sorbent, the activated PNS exhibited appreciable sorption for Pb, Cr and Ni metals ions (97%, 95% and 94%) respectively from aqueous solution. The chemical and thermal activation of peach nut shells enhances the removal efficiency for all metal ions. From reported data; it was found that the adsorption ability of Pb ions is greater than nickel and chromium.

Keywords: Biosorption; Metal ions; Peach nut shell; Freundlich; Langmuir and Dubinin–Radushkevich isotherms.

Introduction

Environmental pollution is mostly likely associated with solid or aqueous waste discharge from industrial and indigenous sources into water streams. The industrial effluents containing various metal ions are released to water reservoirs which are causing serious health problems due to contamination. Due to vigorous industrialization and urbanization, the concentrations of these metals are escalating in the ecosystem [1]. These toxic metals enter into ecosystem through several anthropogenic activities such as smelting of ores, mining of metal ores, leaching of metal compounds, application of fertilizers and pesticides, geological weathering, use of metal compounds and rubbish soil waste dumps and effluents from various chemical industries [2]. The increase in level of pollution beyond the tolerance level is mainly due to these industrial activities [3, 4].

Lead (Pb) exerts injurious impact on nervous system, reproductive systems, hearing, muscular functioning and skeletal formation [5, 6]. The infants and children are more likely to be affected due to their more vulnerability to lead poisoning [7, 8]. The fundamental functional groups (–OH, –S–S–, –COO, –SH, $-OPO_3H$, and –NH) in proteins are poisoned by heavy metal ions which are adversely affecting the living systems. The replacement of Ca^{2+} by Pb^{2+} ions decreases the mechanical strength of bones [9]. Chromium has beneficial and important role in certain metabolic processes [10, 11] but excessive exposure to Cr(VI) compounds is carcinogenic and cause digestive tract and lung cancer [12–15]. Nickel is extensively used in various commercial industries and its intake through contaminated water has been found to be very toxic and its carcinogenic effect has been reported especially in male mice [16].

Several techniques have been employed to purify the waste water such as lime precipitation, coagulation, floatation, sedimentation, filtration, biological and membrane processes but these methods are not economical feasible due to their high running cost, incomplete removal of metal ions, accumulation of toxic sludge and continuous input of chemicals. Among all these methods, biosorption is considered to be better than traditional techniques due to being highly efficient economical and producing less sludge. Therefore nowadays plant materials are being utilized for purification of contaminated water [17–19]. A large number of biosorbent have been investigated for their metal- binding capacity under various conditions, for example, agricultural waists , such as rice straw, coconut husks, waste coffee powder, dried plant leaves, wool, cotton seed hulls, waste tea, cork biomass [20], cashew nut shell [21] and peach nut shell [22].

Keeping in view the potential of peach nut shell for the removal of endosulfan from aqueous solutions [23] present study was carried out to investigate the sorption efficiency of PNS for removal of the toxic metal ions from water steams. Peach nut seeds are agro waste and excessively available in Pakistan. Therefore peach nut shell are most suitable due to its dual advantages, one way is the utilization of agro waste and on other hand as a biosorbent for removal of toxic metals from aqueous streams.

Materials and Methods

Apparatus

Electrical sieve shaker (Ro–Tap type, 20–200 rpm), surface area analyzer (Costech, Sorptometer Kelvin 1042), Electric centrifuge, Thermo Electron Corporation PRECISION water bath B. Bran Scientific and Instrument Co. 80–1, Atomic Absorption Spectrophotometer (Shimadzu, AA–760).

Preparation of biosorbent material (PNS)

The PNS were collected from district Sargodha (Punjab), washed and dried in an oven at a temperature 378 K. after drying thoroughly the samples were ground and sieved to particle sizes ranged between 50-200 µm in an electrical sieve shaker (Ro–Tap type, Stuart Scientific wrist–action Shaker (Galen Kemp No. 350–010). The purified samples were stored in desiccators.

Surface area analysis

Surface area of sorbent was calculated by BET (Brunauer, Emmett and Teller) method using surface area analyzer. The N_2 and He gas was used as standard and carrier respectively [24].

Analysis of metal ions

Atomic Absorption Spectrophotometer (Shimadzu, AA–760) was used to calculate the metals ions in the solution before and after each addition of sorbent. The system was equipped with deuterium arc lamp with background correction.

Activation of sorbent

For chemical activation, the sorbent was treated with nitric acid and potassium nitrate whereas for thermal activation, the sorbent was heated at 473 K for 8 h. The sorption efficiency of treated and untreated (PNS) was compared Fig. 1.

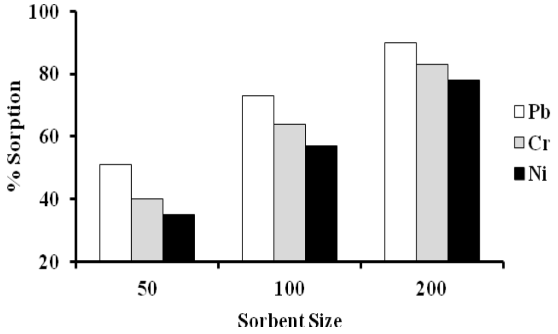


Figure 1. **Effect of sorbent size (µm) on percent sorption**

Batch sorption

The batch adsorption technique was used to measure the metal ions uptake by treated and untreated samples. The samples of metal ions solution were agitated at 100 rpm using Galen Kemp No. 350– 010 Stuart Scientific wrist–action Shaker at 303 ± 1 K for 10– 50 min. The metal ions solution without the sorbent was taken as standard. The similarity in results between standard and treated sample indicates that no loss in metal ions concentration was detected during contamination. The sorption of metal ions was calculated by sorption percentage, using separation factor α and distribution coefficient (R_d) by following equation,

$$\% Sorption = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

Where C_i = initial concentration C_e = equilibrium concentrations of metal ions in mol/L

$$R_d = \frac{C_{ads}\left(mol\, g^{-1}\right)}{C_e\left(mol\, dm^{-3}\right)} \times \frac{V\left(cm^3\right)}{W\left(g\right)} \qquad (2)$$

C_{ads} = amount of metal ions adsorbed by PNS (mol/g), where V is volume of solution,

W= mass of activated sample

$$\alpha = \frac{R_d\left(Metal\, ions\right)}{R_d\left(Metal\, ions\, added\right)} \qquad (3)$$

R_d = distribution ratio (liquid and solid phases).

Results and Discussion

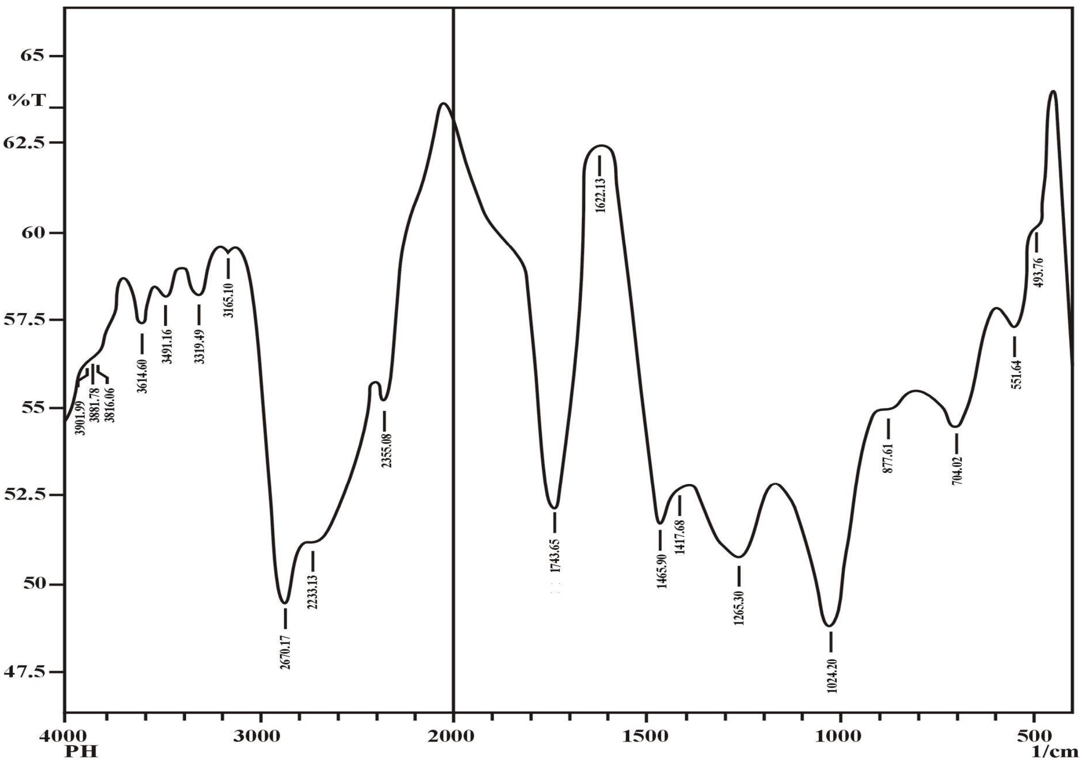
The calculated surface area (366.74 m^2 g^{-1}) and pore volume (495.37 m^2 g^{-1}) of activated material PNS sample was much higher compared to raw sample with surface area of 1.16 m^2/g and total pore volume of 0.001 m^3/g (Table 1). This difference might be due to difference in methodologies (chemical or thermal) applied for activation that significantly affected the surface area, pores volume and its micro porous structure [25]. The chemical treatment increases the surface area and pores volume of sorbent and thermal activation at 473 K for 8 h probably produces a micro porous surface in sorbent which is considered to be responsible for the enhancement of the sorption ability [26, 27].

Table 1. **Pore diameter and pore area of PNS by BET method (both raw & activated).**

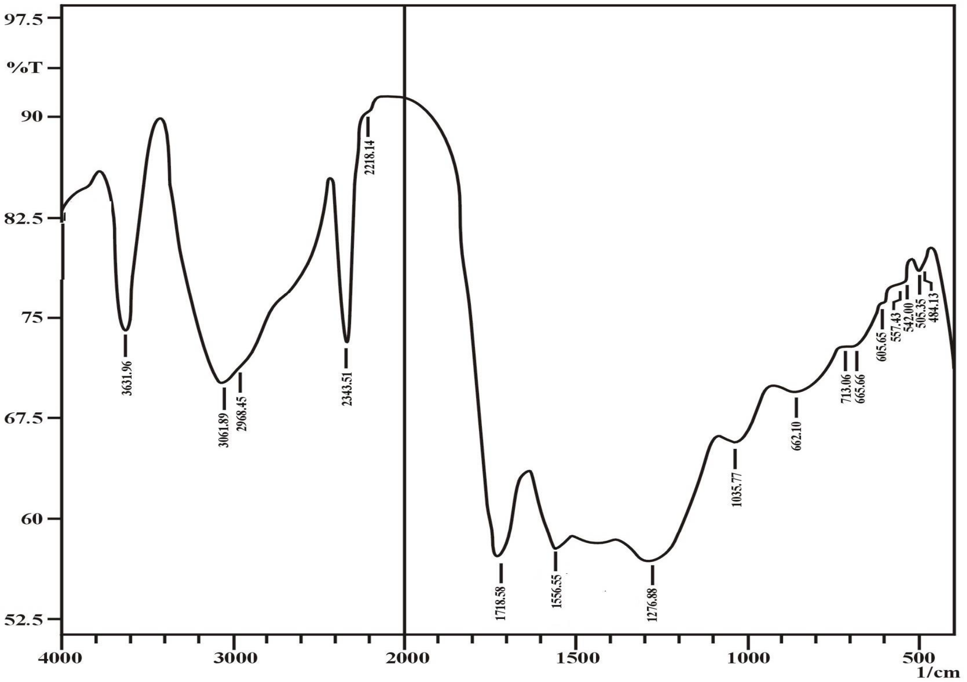
Sorbents	Average Particle size (µm)	Pore area (m^2g^{-1})	Average Pore Valuem (m^3g^{-1})
Raw Sample	200	1.16	0.001
Activated Sample	200	366.74	495.37

Effect of particle size of sorbent on percent sorption

The adsorption potential of sorbents of different particle size was determined for 50, 100 and 200 µm and the results showed that the adsorption capacity increases with increase in size e.g. it was found to increase ~19 % for 100 µm and ~ 42 % for 200 µm. The maximum adsorption ability was shown by sorbent having particle size 200 µm; therefore this size was selected for further studies. The increase in sorption potential due to decrease in mesh size (Fig. 2) might be attributed due to increase in pore size on adsorbent [28].



FT-IR Spectrum of sorbent (PNS)



FT-IR Spectrum of treated sorbent (PNS)

Figure 2. **FT–IR Spectra of raw and treated PNS**

Activated and raw sorbent

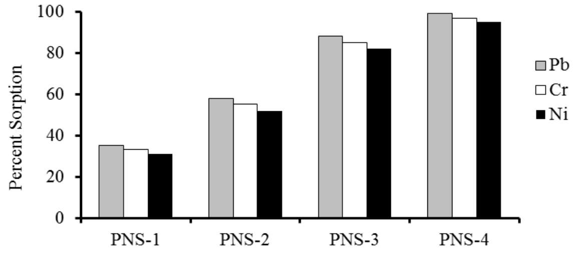
The presence of several peaks in FT–IR spectrum given in Fig. 2, of the adsorbent reveals that it has complex nature having different functional groups. The significant difference in FT–IR spectra (Table 2) of PNS & PNSA is due to appearance of some new peaks responsible for sorption. The existence of free and intermolecular bonded hydroxyl groups in activated sorbent is indicated by peak around 3065.90 cm^{-1} which is absent in spectrum of untreated sample. Similarly, involvement of lignin aromatic groups having peak 1744.66 cm^{-1} for C=O group (migrated to 1718.58 cm^{-1}) shows a clear role in the adsorption of metal ions. The appearance of peak at 2968.45 cm^{-1} in the spectra of activated sample might be attributed to C–H stretching of aliphatic carbon or due to deformation in – CH_2, – CH_3 groups. The observed small peak around 1556.55 cm^{-1} in IR spectrum of activated sample can be attributed to carboxyl ate group or ether which are missing in the spectrum of raw sample, suggesting that its higher sorption potential is due to its structural modifications. In activated and raw sample, the peaks at ~ 1036 and 1025 cm^{-1} respectively are expected due to overlapping of C–O stretching, C–O–C stretching and –OH bending modes of ether, phenolic and alcoholic groups, and a wide peak of Si–O–Si linkage is at ~ 878 cm^{-1} compare to activated PNS. These peaks are more pronounced in raw samples and strong vibrational frequencies in untreated PNS have been reduced by activation thus the adsorption potential of activated PNS samples have increased compared to raw PNS [29].

Table 2. **FTIR Study of sorbents.**

	Absorbance (cm^{-1})				
Adsorbents	**O–H**	**C–H**	**C=O**	**C–O–C**	**Si–O–Si**
Raw sample	——	——	1743.65	1025	878
Treated sample	3061.89	2968.45	1718.58	1036	——

Effect of thermal and chemical treatment on % sorption

The removal efficiency of both samples were noted and it was found that the sorption potential of raw sample for selected metal ions has significantly increased after activation (chemical and thermal treatments). These type of treatments might play a role in improving the surface area as well as pore volume (Fig. 3).



PNS-1 (peach nut shell treated with water)
PNS-2 (peach nut shell treated with HNO_3)
PNS-3 (Peach nut shell treated with HNO_3, KNO_3)
PNS-4 (Peach nut shell treated thermally at 473K)

Figure 3. **Effect of thermal and chemical treatment on the % sorption, conc. of metal ions, (Pb = 0.49, Cr = 1.93 & Ni = 1.72) ×10^{-4} mol/L, sample = 0.2 g, shaking speed =100 rpm, agitation time = 20 min, pH = 6 at 303 K**

Effect of pH on removal efficiency

The sorption of Pb, Cr & Ni metal ions was studied over a range of pH (1–10) to find the optimum pH. It plays a vital role for adsorption while keeping other parameters constant. The adsorption efficiency of activated sample was increased by increasing the pH and was found to be maximum at pH 6 but no increase in sorption was observed by further increasing the pH of medium. Therefore all further studies were conducted at pH 6 (Fig. 4).

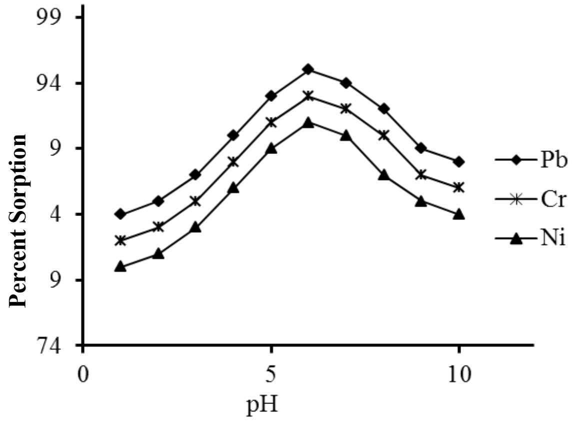


Figure 4. **Effect of pH on sorption, sorbent dose = 0.2 g, Pb, Cr and Ni solutions (4.81, 8.92, 15.70)× 10^{-5} M, agitation time = 20 min at 303 K.**

Effect of concentration of sorbate on removal efficiency

The effect of initial concentration (Ci) of sorbate on removal efficiency was studied. The decrease in binding percentage was observed by increase in initial concentration of sorbate with corresponding decrease in distribution coefficient 'Rd' (Fig. 5). This effect was might be due to free availability of surface area of sorbent for adsorption of metal ions at low concentration and hence greater is the removal of metal ions from the sample solution. In case of higher concentration, this ratio becomes relatively low; hence the percentage removal was decreased [30].

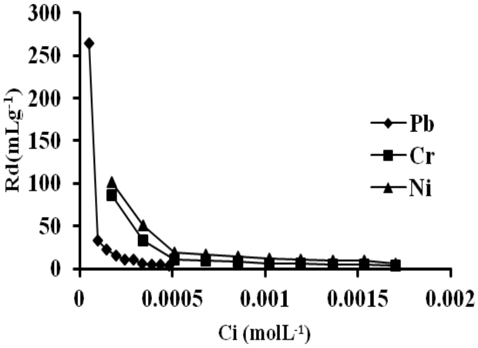


Figure 5. **Effect of initial conc. of metal ions, Pb = 0.480–4.80×10^{-4} M, Cr = 1.920–19.20×10^{-4} M and Ni = 1.70-17.0×10^{-4} M, Activated sample = 0.6 g, pH= 6, shaking speed =100 rpm at 303 K**

Effect of adsorbent loading weight

The sorbent dose was changed from 0.05 to 1.0 g to find its effect on metals ions sorption by keeping other optimized parameters constant (Fig. 6). It was found that the % removal of metal ions was increased by increasing the sorbent dose from 0.05 – 0.6 g and no further increase in sorption potential was observed by further increasing its dose from 0.6 –1 g. From this study it was found that the increase in adsorption was due to availability of more and more adsorption sites at relatively low concentration for metal ions up to 0.6 g but further increase in sorbent dose, no significant effect was seen. This is suggested that at higher concentration aggregation and overlapping of adsorption sites decreases the number of ions adsorbed per unit mass (sorption density) above equilibrium.

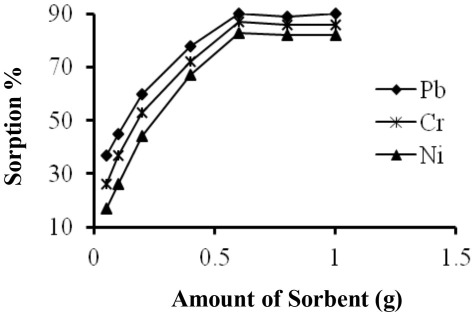


Figure 6. **Effect of sorbent dose (0.050 to 1.00 g), activated sample = 0.20 g, conc. of Pb, Cr & Ni = 10 ppm, shaking speed =100 rpm for 20 min**

Effect of shaking time on removal efficiency

The investigation of the influence of shaking time on the percent adsorption of metal ions was made at room temperature by changing the shaking time from 5 to 50 min keeping other parameters constant (Fig. 7). The experimental data revealed that the adsorption was increased by increasing the shaking time and became constant after about 30 minutes. The increase in adsorption competency of activated PNS could be credited to availability of functional groups (adsorbing sites) on the adsorbent surface. After equilibrium, sorbent surface was saturated with metal ions and further adsorption became difficult due to repulsion between adsorbed metal ions and the metal ions present in solution. So no further increase in adsorption was observed after attaining the equilibrium state.

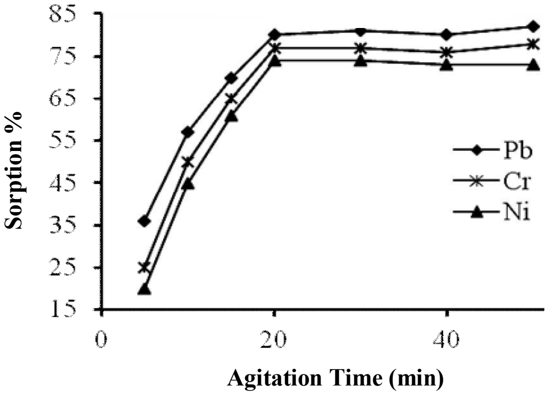


Figure 7. **Effect of agitation shaking time at shaking speed of 100 rpm, Agitation time (5 to 50 min), PNSA = 0.2 g of, conc. of Pb, Cr and Ni solutions = 10 ppm**

Effect of shaking speed on removal efficiency

In order to investigate the effect of shaking speed on the percentage adsorption of metal ions, the activated samples were stirred at speed ranging from 25 to 200 rpm (Fig. 8). The percentage sorption was increased on increasing the shaking speed upto100 rpm and no further change in adsorption was observed on further increase in shaking speed. The increase was due to fast rate of diffusion of metal ions from metal ions solution onto activated sample due to decrease in thickness of liquid boundary layer and enhancement in turbulence at higher speed. On reaching at equilibrium state, % adsorption was at its climax and no further increase in sorption was observed. So this speed was taken as optimum speed

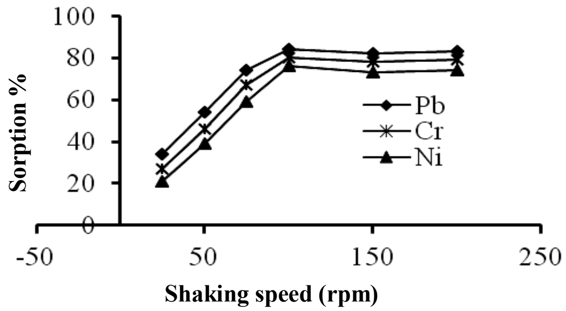


Figure 8. **Effect of shaking speed, Shaking speed (25 to 200 rpm) PNSA = 0.2 g , 20 cm^3 solutions of Pb, Cr and Ni ions (10 ppm) t= 20 min at 303 K**

Isothermal studies

The effect of sorption isotherm on amount of sorbate and its degree of accumulation on sorbent surface at constant temperature was evaluated by employing Freundlich, Langmuir and Dubinin–Radushkevich (D–R) models.

Freundlich isotherm

It gives an empirical expression encompasing the surface heterogeneity. The freundlich isotherm was tested by a linear equation,

$$\log C_{ads} = \log C_m + \frac{1}{n} \log C_e \qquad (4)$$

where C_{ads} (mol/g) and C_e (mol/L) are sorbed and equilibrium concentrations of sorbate on the sorbent surface at equilibrium, where C_m (m mol/g) represents the multilayer sorption capacity of sorbent and $\frac{1}{n}$ measures the intensity of sorption. By plotting a graph between Log C_{ads} and Log Ce for all metal ions solution, a straight line was obtained (Fig. 9). The slope of this line gives $\frac{1}{n}$ whose values for Pb, Cr and Ni ions were found to be 0.311, 0.361, and 0.390 respectively. The values <1 indicates better sorption.

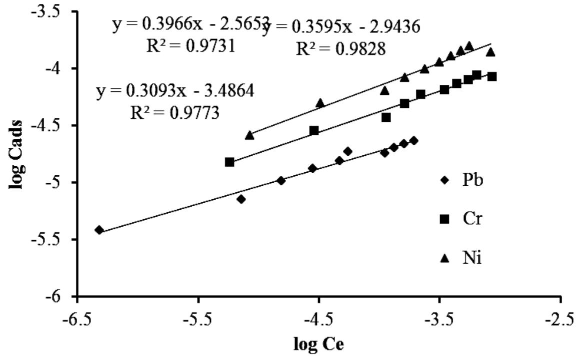


Figure 9. **Freundlich isotherm, activated sample = 0.2 g, sorbate concentration (4.80– 48, 8.90 –89 and 15.70 –157) 10^{-5} M solutions, agitation time = 20 min at 303 K**

Langmuir isotherm

This model describes the monolayer sorption at appropriate homogeneous sites and was applied to sorption data [31]. The data was tested by applying following relationship in linear form,

$$\frac{C_e}{C_{ads}} = \frac{1}{Q_b} + \frac{C_e}{Q} \qquad (5)$$

Where Q represents the maximum sorption capacity in mmol/g, and b is heat of adsorption at constant temperature in L/mol. This graph (Fig. 10) indicates that the Langmuir sorption model is followed very well by the sorption data. The parameters Q and b were calculated using values of slope and intercepts of the plot. A dimensionless constant, separation factor, RL was applied to given data to find the favorability of adsorption isotherm [32]. If R_L >1; the isotherm is favourable, if 0 $<R_L<1$; unfavorable, if $R_L = 1$; linear and irreversible if $R_L = 0$; these are essential characteristics for Langmuir isotherm [28] and these can be calculated in concentration ranges of 0.0000480 – 0.00048, 0.0001920 – 0.00192, 0.000170 –0.00170 mol/L for Pb, Cr and Ni ions respectively, by putting the relationship,

$$R_L = \frac{1}{1+b\,C_i} \tag{6}$$

Where 'b' is called Langmuir constant (L/mole) and C_i is termed as the initial concentration of sorbate (mol/L). The R_L values in the range (0.040 – 0.280, 0.060 – 0.401 and 0.06 – 0.38) indicate that the sorption is very favorable at lower concentrations of Pb, Ni and Cr ions respectively.

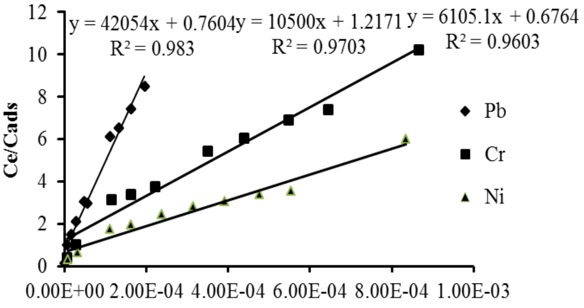


Figure 10. **Langmuir isotherm, Activated sample = 0.2 g, (4.80 – 48, 8.90 – 89 and 15.70 –157) 10^{-5} M solutions of sorbate, agitation time = 20 min at 303 K**

Dubinin Radushkevich (D-R) isotherm

This model helps in determining the apparent energy of adsorption, porosity of adsorbent towards the adsorbate and this model does not assume a homogeneous surface or constant sorption potential (Fig. 11). The application of D–R isotherm to the sorption data in linear form is,

$$\ln C_{ads} = \ln X_m - \beta\, \varepsilon^2 \tag{7}$$

Where C_{ads} (mol/g) represents the equilibrium concentration of sorbate on the surface of the sorbent, sorbent maximum sorption capacity is given by X_m (m mol/g); β (k J^2/mol^2) is a constant relating to energy where ε is Polanyi sorption potential.

$$\varepsilon = RT \ln\left(1+\frac{1}{C_e}\right) \tag{8}$$

Here R= gas constant in kJ/mol K, T= absolute temperature in Kelvin, C_e = equilibrium concentration of sorbate in solution. The plot of $\ln C_{ads}$ versus ε^2 for the sorption data yields a straight line. The linear plot (Fig. 10) indicates that D–R isotherm was obeyed over all concentrations range of Pb, Cr & Ni metal ions. The β and X_m were calculated from slope and intercept of graph (Table 3).

Table 3. **Values of Freundlich Constants for metal ions on activated sample.**

z	R^2	n	Cm (mmol g^{-1})
Pb(II)	0.977	3.23341	0.32626
Cr(II)	0.982	2.78184	1.13861
Ni(II)	0.973	2.72084	2.52114

Kinetics of sorption

Kinetic models were applied to study the adsorption kinetics for Pb, Cr & Ni. The Lagergren equation [33] was applied to obtain the kinetic data (Fig. 11).

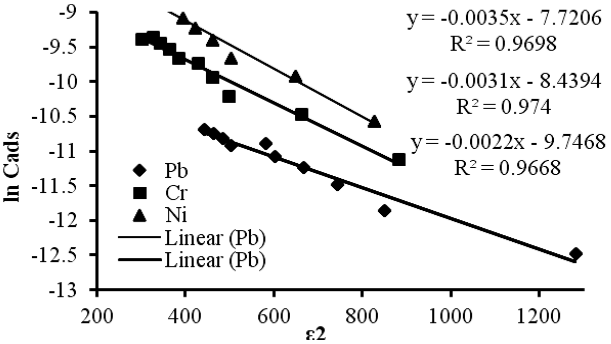


Figure 11. **(D–R) isotherm, Activated sample = 0.2 g, concentrations of sorbate (4.80–48, 8.90–89 and 15.7–157) 10^{-5} M solution, agitation time = 20 min at 303 K**

$$\ln(q_e - q_t) = \ln q_e - kt \tag{9}$$

Where 'k' is the 1st order rate constant (min^{-1}), whereas q_e and qt are the equilibrium and sorbed concentrations (µmol/g) of metal ions at time 't' respectively.

The equation was tested by plotting a graph between $\ln(q_e - q_t)$ versus t, and a straight line was obtained for all metals ions (Fig. 12). The values of k for Pb, Cr and Ni metals ions 0.13, 0.16 and 0.15 min^{-1} respectively corresponds with 1st order rate constant and were computed from slope of the corresponding plots.

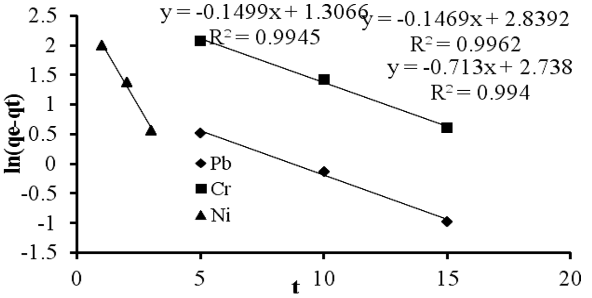


Figure 12. **Legergren plot, activated sample = 0.6 g, concentration of sorbates (0.480 –4.8, 1.920 –19.2, 1.70 –17.0) × 10^{-5} M solution, agitation time = 20 min at 303 K**

Morris–Weber equation was used to find intra–particle diffusion rate constant R_{id} (µmol/g min) [34, 35].

$$qt = Rid\ t^{1/2} \qquad (10)$$

Sorption data was tested by plotting a graph between q_t versus $t^{1/2}$, and a straight line was obtained (Fig. 13) showing that sorption followed partial intra–particle diffusion mechanism.

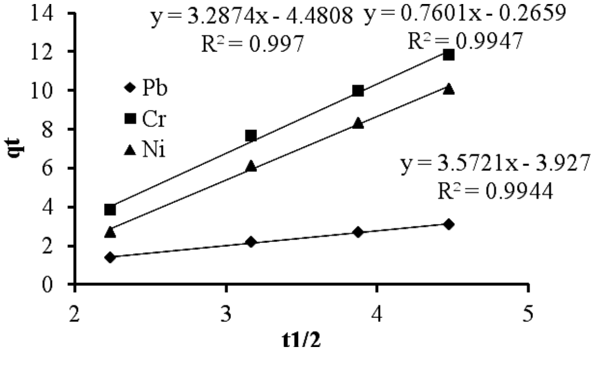


Figure 13. **Morris–Weber Plot, Activated sample = 0.6g, concentration of sorbate (0.48 – 4.8, 1.92 –19.2, 1.70 –17.0) × 10^{-5} M solution, agitation time = 20 min at 303 K**

Conclusion

This study shows that activated PNS exhibited appreciable sorption for Pb, Cr and Ni metals ions (97%, 95% and 94%) respectively from aqueous solution even at very low concentration of sorbent.

The chemical and thermal activation of PNS enhances the removal efficiency for all the metal ions and from the reported data; it was found that the adsorption ability of Pb ions was greater than nickel and chromium.

Economic point of view, the chemical activation appears to be a better strategy for increasing the size of pores already present as well as creating new pores in the substrate. The treated carbonaceous material demonstrated better adsorption than untreated sample. The FT–IR study has indicated the presence of some well-known adsorption sites (carbonyl, carboxylic acid, hydroxyl, and ether groups) in PNS structure.

The Freundlich, Langmuir and D–R model described more precisely the partitioning behavior between solid and liquid phases by evaluating the sorption efficiency and equilibrium data was fitted well to Langmuir isotherm and coefficient of determination was found very close to 1. Kinetic study revealed that during adsorption, 1st order kinetics and intra particle diffusion mechanism was dominant and separation factor showed that reaction was favorable, feasible and spontaneous.

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