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Adsorption of Cd(II) from Aqueous Solution by Activated Carbon Prepared from *Vitex negundo* Stem

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ABSTRACT

This study reports the removal of cadmium from wastewater in batch mode, using Vitex Negundo stem. The activated carbon prepared from VNC modified with activating agent H_2SO_4. The adsorbents were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX).The results of batch experiment showed that the cadmium removal was dependent on pH, Cd(II) ion concentration, adsorbent dose, size and temperature. The highest cadmium adsorption was found at pH = 6.0, initial Cd(II) concentration = 100 mg/L, adsorbent dose = 200mg, size= 0-53µ at temperature= 33±2^{0}C. The optimum conditions for adsorption studies are calculated and it concludes that the activated carbon exhibits a good adsorption potential for cadmium ions. The results indicate that the carbon prepared from VNC-1 activated could be used to effectively adsorb Cd (II) ions from aqueous solutions.

Keywords: Adsorption; Cadmium (II) ions; Batch studies; SEM; EDX; FTIR; XRD

INTRODUCTION

With the rapid development of modern industries, the environment has faced more and more contamination than in the past. It is well known that heavy metals present in surface waters are extremely dangerous to environmental and human health because unlike organic pollutants they are not biodegradable and must be removed to prevent their accumulation. Industrial discharges, mainly from mining, metal finishing, pulp industries, petroleum refining industries pigment and dye industries, are responsible for heavy metal contamination [1, 2].

Lead and cadmium are the most toxic non-essential heavy metals present in the environment. Lead poisoning in humans causes severe damage to the kidney, nervous system, reproductive system, liver, brain and causes death. Severe exposure to lead has been connected with sterility, abortion, stillbirths, and neonatal death [3,4]Chronic exposure to elevated level of cadmium is known to cause renal dysfunction (Fanconi syndrome), bone degradation (itai–itaisyndrome), cancer, hypertension, liver damage, and blood damage [5]Several methods are available to remove toxic metals from aqueous waste streams, such as chemical precipitation, electrolysis (membrane separation), solvent extraction, reverse osmosis, ion exchange and adsorption. Among these techniques, reverse osmosis, is very effective, even though it is a cost-prohibitive process as the membranes get easily spoiled requiring frequent replacement. Chemical precipitation is not very suitable when the pollutants are present in trace amounts and also a large amount of secondary waste is produced.

Ion exchange is an expensive and sophisticated method for the removal of trace quantity of metal ions. Solvent extraction or electrolytic processes are also available but they are considered to be cost-effective. Hence, adsorption is probably one of the most attractive, simple and efficient processes and consequently, it is commonly used in industry, because of its simple and efficient application [6-8] Although commercial activated carbon, with high surface area, porous character and high adsorption capacity, has made it as a potential adsorbent for the removal of heavy metals from industrial wastewater, it is not being recommended because of the high operation costs. Thus, there is a growing demand to find low-cost and efficient adsorbent for the adsorption of heavy metal ions [9]. Hence it is of great importance to search new materials to replace activated carbon. The materials developed for this purpose range from industrial wastes to agricultural waste products [10-13].with the emergence of nanoscience and technology in the last decade, research has been initiated to exploit the unusual and unique properties of nonmaterial for environmental remediation [14-16].

Although research in the area of heavy metal removal by low cost adsorbent is underway, very little attention has been dedicated to this important issue. The objective of present work is to study the adsorption of Cd(II) ions from aqueous solutions onto Vitex Negundo Stem Via low cost adsorbent. The effects of temperature, pH, contact time and concentration on metal ion adsorption efficiency were examined. The adsorption isotherms, kinetics and thermodynamic parameters were deduced from the adsorption measurements.

MATERIALS AND METHODS

Reagents and materials

$Cd(NO_3)_2$, hydrochloric acid (HCl) and sodium hydroxide (NaOH) with the highest purity available were purchased from Merck(Darmstadt, Germany). Double-distilled water was used in all experiments. Stock solution (1000 mg L^{-1}) of The stock solution of Cd(II) 2.7441g/$dm^3$was prepared from Cd(II).$8H_2O$. The solutions of different initial concentrations were prepared by diluting the stock solution inappropriate proportions. By using this stock solution the desired dilutions were made and used throughout the study [17].

Preparation of adsorbents

The plant chosen for the preparation of activated carbon is *vitex negundo* stem. Chemically activated carbon can be prepared by dipping the plant material into H_2SO_4 (50%). The plant materials were kept for 24 hours, at the end of the 24 hours the soaked materials were removed and dried in oven at 110^0C for 4 hours. The dried samples are made to activate in a muffle furnace at 600^0C for 3 hours in the absence of air. The activated samples were cooled and washed with distilled water until the pH of washed water become pH 7. The activated samples are then crushed; sieved sample was stored in air tight plastic container. Named as VNC-1used for further characteristics work.

Characterization of adsorbents

The order to characterize the surface structure of activated charcoal HR-SEM in F E I Quanta FEG 200 ZEISS analysis was carried out. The surface morphology involved in metal adsorption, XRD was performed on X'Pert-Pro, PANalytical diffractometer operated at 30 kV/30 mA, to determine the material using CuKa1 radiation with wavelength of 1.54 A° in the wide angle region from 10^0 to 80^0 on2θ scale. VNC-1 and Cd (II) loaded/VNC-1. The functional group were analyzed using FT-IR spectra of the samples were recorded in the range of 400–4000 cm^{-1} shimadzu spectrometer.

Batch adsorption studies

Batch adsorption equilibrium experiments were conducted for the adsorption of lead on activated carbon of VNC-1 as a function of pH, initial Cd(II) concentration, adsorbent dose and contact time by adding 0.2 g of dried carbon to 100mL of lead solution with different concentrations in 250-mL Stopperd reagent bottles at a constant shaking. All the experiments were carried out at room temperature 33±2^0C. For studying the influence of pH on the adsorption of Pb(II), the experiments were conducted at various initial metal solution pH values of 3–7. The pH of each solution was adjusted to different values with either0.1 N NaOH or 0.1 N HCl. All experiments were carried out by adding 50mL of metal solution and adsorbent in an Erlenmeyer flask and made for constant stirring for 210 min. At the end of the each experiment, the solution was filtered and the filtrate was titrated with EDTA solution. In order to reproduce the results, during the adsorption, a rapid equilibrium established between adsorbed metal ions on the active cites of adsorbent (qe) and unabsorbed metal ion in the solution. The amount of adsorption at equilibrium (qe) (mg/g) and the percentage adsorption (%) were computed as follow

$$\text{Adsorption capacity } (q_e) \text{ (mg/g)} = \frac{(C_0 - C_e)\,V}{X}$$

$$\text{\% Percentage Adsorptiom (\%)} = \frac{(C_0 - C_e)\times 100}{C_0}$$

Where C_0 and Ce represented the initial and equilibrium concentrations (mg/L),
V is the volume of solution and X the weight of adsorbent (g).

RESULTS AND DISCUSSION

Characterization of adsorbent

SEM (Scanning Electronic Microscopic):

The surface texture and morphology of VNC-1 and VNC -1 / Cd (II) was determined using scanning electron micro-graph. The availability of pores and internal surface, which is a requisite for a potential adsorbent, is clearly displayed in the SEM and EDX picture of the before adsorption of VNC-1 and after adsorption of VNC-1/Cd(II).

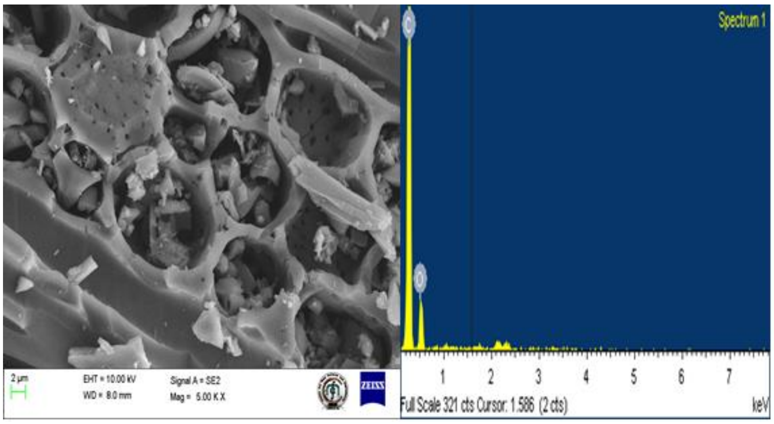

Figure 1: SEM and EDX micrograph of the VNC-1

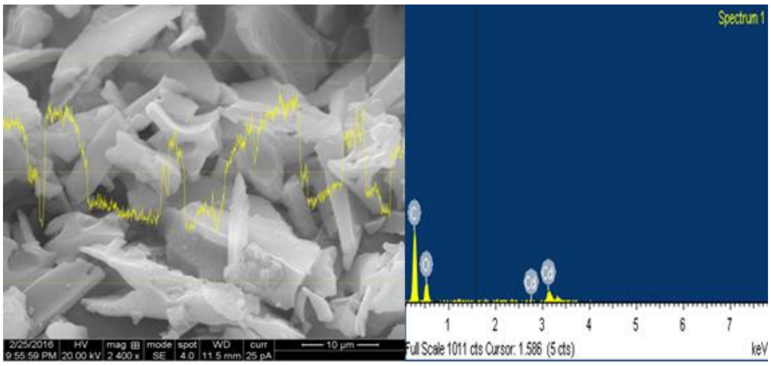

Figure 2: SEM and EDX Image of VNC-1 after Cd(II) adsorption

Spectral studies

The functional groups present in the active sites of an adsorbent are examined using FTIR spectroscopy. The functional groups present in the surface of the adsorbent are attributable for attracting the metal ion present in the solution. The functional present in VNC-1and Cd loaded/ VNC-1shown in fig-3. The figure illustrates that peaks obtained in the range of 3340cm^{-1} reveals the acidic hydroxyl group present in the surface and the peaks at 3340-2920 cm^{-1} shows the presence of O-H groups present in the adsorbent. The peaks observed at 2919-2686 cm^{-1} indicates the presence of –CH and –CO groups and the peaks obtained at 1589-1585 cm^{-1} shows the presence of the N-H group as primary amines and –C-C group. The peaks at 1382-1353 cm^{-1} indicates the presence of CH groups on the surface of the VNC-1.then-C-Cl groups of alkyl halide present in the range of peaks obtained from 850-550 cm^{-1}. The adsorbents loaded with Cd(II) shows a similar FTIR spectrum as that obtained with an unloaded adsorbent, except that the bands had shifted to higher or lower values as shown in figure. The shifting of band due to the Cd(II) adsorption. Thus, the FTIR analysis revealed that the functional group like –OH, C-H bending, and C=O, COO-, O-H groups were mainly responsible for the adsorption.

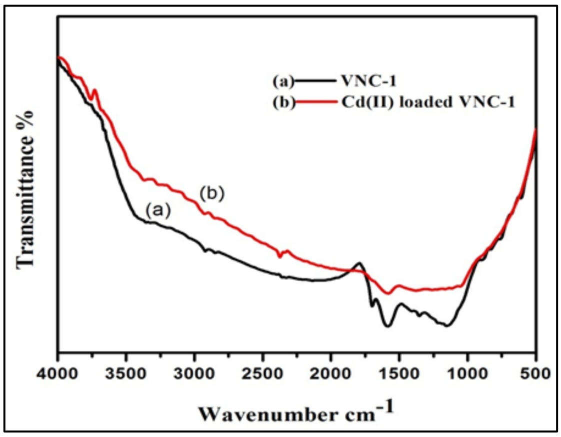

Figure 3: FT-IR spectrum of before and after adsorption of Cd(II) ion

X-Ray Diffraction (XRD)

X-ray diffraction (XRD) patterns of the powders were recorded at room temperature. The XRD pattern has a highly porous structure with sharp edges $2\theta = 25.42^0$ was appeared in VNC-1 after adsorption Cd(II) in VNC-1 the peak appeared prepared carbon gets slight diminished which shows an evidence of adsorption of metal ion. The powder XRD data active sites and 2θ as well as the *d* values present in VNC-1 and Cd (II) loaded VNC-1 carbons are shown in figure 4.

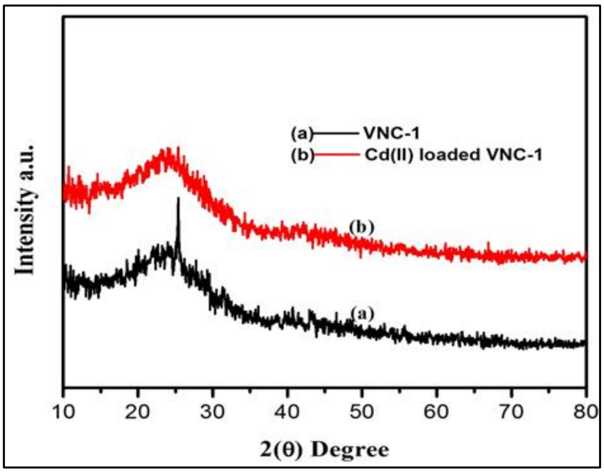

Figure 4: XRD Spectrum of VNC-1 before and after adsorption of Cd(II)

Effect of initial concentration of Cd(II)

The effect of initial cadmium concentration in the range of 100 to 500mg/L on adsorption was investigated (Figure 5). Along with pH all parameters were kept constant in this study. It is evident from the Fig.5 that, as the concentration of Cd(II) was increased, the amount adsorbed was increased but, there was decrease in percentage removal. It is because, the initial cadmium concentration provides the necessary driving force to overcome the resistances to the mass transfer of cadmium between the aqueous phase and the solid phase. The increase in initial cadmium concentration also enhances the interaction between cadmium and VNC-1 i.e. adsorbent. Therefore, an increase in initial concentration of cadmium enhances the adsorption uptake of cadmium and results in higher adsorption, while the adsorption was carried out for fixed number of active sites, there was decrease in percentage removal of Cd(II). The amount adsorbed of Cd(II) was increased from 42.15 to 105.78 mg/g (Table-1) as the initial metal ion concentration increased.

Table 1: Initial concentration of Cd(II) on amount adsorbed mg/g and removal, % of Cd(II)

S.No	Initial Conc cd(II) mg/dm3	Removal of cd(II) %	q mg/g amount adsorbed
1	100	71.42	42.15
2	200	67.71	70.25
3	300	56.6	84.3
4	400	43.83	89.92
5	500	42.29	105.78

Table 2: Comparison of VNC-1 Cd(II) with conventional adsorbents using the maximum adsorption capacity (q max – mg/g)

No	Adsorbent	q_{max} (mg/g) amount adsorbed	References
1	Orange peel	136.05	[18]
2	Orange peel	293.3	[19]
3	Cashew nut shell	436.7	[20]
4	CAC	238.09	[21]
5	Rattan SAC	149.25	[22]
6	VNC-1	105.78	This study

Effect of adsorbent dosage

Adsorption dosage is one of the vital parameters in the study. The adsorbent dosage i.e. VNC-1 varied from 100−500 mg/dm^3, to study the effect on the adsorption of Cd(II). To study this effect, the concentration of Cd(II) was taken as200mg/dm^3 and other parameters were kept constant. As the amount of adsorbent was increased, the amount adsorbed and percentage removal of Cd(II) was respectively increased. The adsorbent dosage affects directly on the adsorption capacity, as there is increase in dosage more active sites becomes available for adsorbate and it was confirmed from the (Fig.6 and Table-3). The maximum amount of 11.91 mg/g of Cd(II) was adsorbed for 500 mg of VNC-1 and 58.24% Removal of Cd(II) was found, so throughout the study the 500 mg/dm^3 amount of VNC-1 as adsorbent was kept constant.

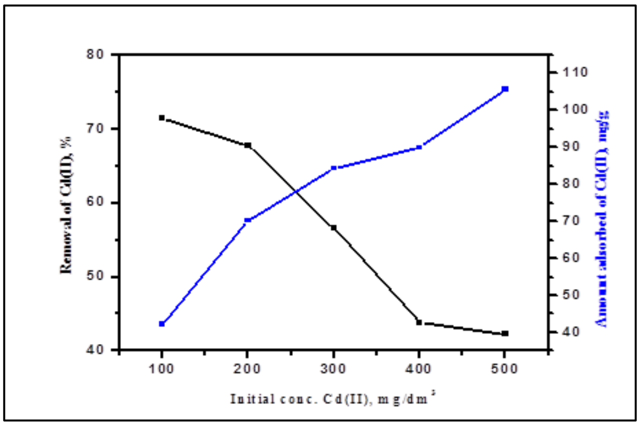

Figure 5: Effect of initial concentration of adsorbent on removal of Cd(II) from aqueous solution Conditions:; adsorbent dose=200mg; Size of adsorbent=0-53µ; pH=6; temperature=33±2°C

Table 3: Effect of adsorbent dosage on Cd(II) removal, % and amount adsorbed, mg/g

S.NO	**Dose of the Cd(II) mg/dm^3**	**Removal of Cd(II) %**	**q mg/g amount adsorbed**
1	100	40	40.46
2	200	44.45	22.48
3	300	48.91	16.86
4	400	51.08	13.2
5	500	58.24	11.91

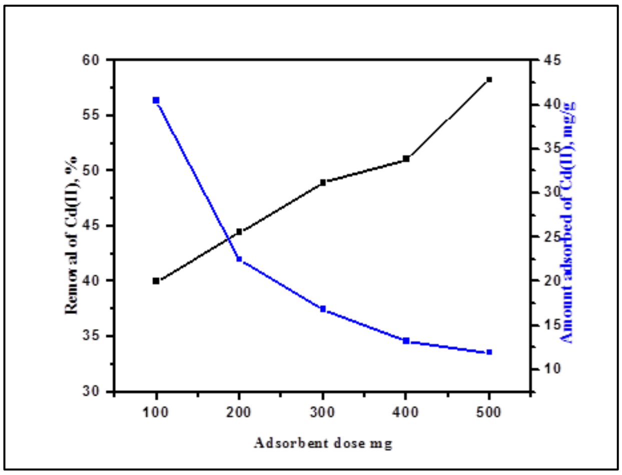

Figure 6: Effect on dose of adsorbent on removal of Cd(II) from aqueous solution Conditions: Cd(II)=100mg/L; Size of adsorbent=0-53µ;pH=6;temperature=33±2°C

Effect of pH

The effect of pH on adsorption of Cd(II) was studied with varying the pH from 3 to 7. The concentration of Cd(II) was taken to be 100 mg/L while the volume of solution was kept to 50mL, at constant temperature 33 ± 2^0C and it was agitated for 4 h at 150 rpm. From Fig.7 (Table -4) it clearly indicates that, the adsorption was significant above pH- 6. For the further study pH 6 was confirmed because, above neutral pH the reaction mixture forms precipitate. The cadmium percentage removal and adsorption capacity was found to be 71.43% and 42.15 mg/g respectively for VNC-1.The pH of the solution was found to have a great effect on the adsorption of Cd(II) ions.

The adsorption increased sharply in the pH ranges 3 to 7 attaining almost a constant value at higher pH. Such results could be attributed on the basis of the change in the carbon surface charge with change in pH of the solution [23].

The lower adsorption capacity observed at low pH may be explained on the basis on electrostatic repulsive forces between positively charged H_3O^+ and Cd(II) ions. At low pH values, the concentration of H_3O^+ is higher than that of Cd(II) ions and, hence, these ions are adsorbed on the active sites of activated adsorbents, leaving Cd(II) ions free in the solution. When the pH was increased, Cd(II) ions would replace with H_3O^+ ions. Competing effect of H_3O^+ decreased with increase of the pH, which increases the adsorption yield of the Cd(II) ions. The adsorption capacity increases with increase in pH value up to 6 and remains constant up to pH 7.0 but we have considered range of pH 6 – 7. As the removal takes place by adsorption as well as precipitation of Cd(II) ions in the form of $Cd(OH)^2$. The decrease in adsorption yields at alkaline conditions can be attributed to the formation of $Cd(OH)^{3-}$ ions taking place as a result of dissolution of $Cd(OH)^{2}$. Due to its amphoter characteristic.the hydrolysis and precipitation of metal ions affect adsorption by changing the concentration and form of soluble metal species available for adsorption. The hydrolysis of Cd(II) ions maybe represented by following reaction,

$$Cd^{2+} + 2nH_2O \leftrightarrow Cd(OH)n^{2-n} + nH_3O^{+} \quad (1)$$

Depending upon the pH of the solution, various species of cadmium can be formed during the hydrolysis. The hydrolysis extent of Cd(II) ions is unimportant up to approximately pH 7.5 and cadmium is in the form of Cd^{2+} ions at this pH. For that reason it can be said that the adsorption mechanisms can be explained on the basis of H_3O^{+}–Cd^{2+} exchange reaction [24].Initial pH of solution varied within the range 1 – 7. This pH range was chosen in order to avoid metal hydroxide precipitation.

Table: 4 Effect of pH on removal, % and amount adsorbed, mg/g of Cd(II)

S.NO	pHof the Cd(II) mg/dm^3	Removal of Cd(II) %	q mg/g amount adsorbed
1	3	57.14	33.72
2	4	61.9	36.53
3	5	65	36.53
4	6	71.43	42.15
5	7	42.85	25.29

Table: 5 Optimum pH values in various Plant and VNC-1 Cd (II) adsorption systems

No	Adsorbent	Optimum pH	References
1	Coffee grounds	7	[25]
2	Wheat straw	6	[26]
3	Pineapple peel fibre	7.5	[27]
4	Castor seed hull	6	[28]
5	Potato Peels	6	[29]
6	Oyster mushroom, button mushroom and milky mushroom	6	[30]
7	VNC-1	6	This study

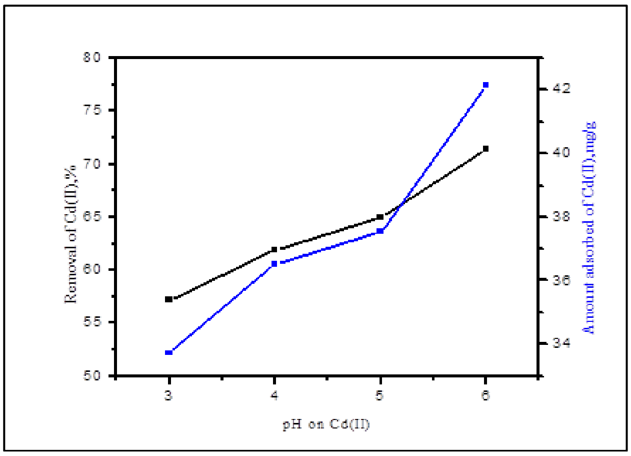

Figure 7: Effect of pH on removal of Cd(II) from aqueous solution Conditions: Cd(II)=100mg/L; adsorbent dose=200mg;Size of adsorbent=0-53µ; temperature=33±2°C

Effect of particle size on Cd(II) removal

Adsorption is a process of surface controlled phenomenon. The percent removal of Cd(II) decreased with increasing adsorbent particle size as shown in fig-8. The higher adsorption occurred in smaller adsorbent particle size is attributed due to the smaller particles gives large surface areas offering a comparatively larger and more accessible surface area and hence, there was an increase of adsorption is found as the size of the particle gets decreased. Thus, the adsorption equilibrium of cadmium is found to be (75.00%) at180 min with size 0-53µ and increasing the adsorbent particle size to 53-106µ and 106-300µ and 300 -500µ leads to decrease of percent removal by (63.16%). For optimum condition, low particle size (0-53µ) was used for further experiments. Table 6.

Table: 6 Effect of size on Cd(II) removal, % and amount adsorbed, mg/g

S.NO	Size of the Cd(II) mg/dm3	Removal of Cd(II) %	q mg/g amount adsorbed
1	53	75	42.15
2	106	70	39.34
3	300	66.66	36.78
4	500	63.16	32.72

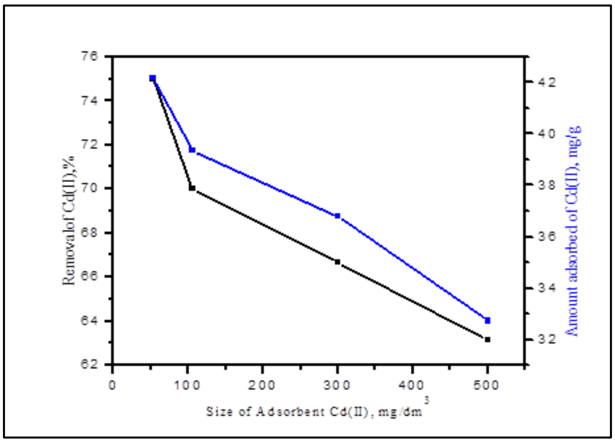

Figure 8: Effect of Size of adsorbent on removal of Cd(II) from aqueous solution Conditions: Cd(II) =100mg/L; adsorbent dose=200mg; pH=6; temperature=33±2°C

Effect of temperature

The adsorption of Cd(II) on VNC-1 was investigated as a function of temperature and maximum removal of Cd(II) was obtained at 35^{o}C. Experiments were performed at different temperatures of 35, 40, 45, 50 and 55^{o}C for the initial Cd(II) concentrations of 100 and 500 mg/L at constant adsorbent dose of 0.2 g/L and pH of 6. The adsorption decreased from 61.11 to 58.76 and 53.26 to 50.55and 47.77% for the initial lead concentrations of 100 and 500 mg/L respectively with the rise in temperature from 35 to 55^{o}C (Fig.9). This is mainly due to the decreased surface activity suggesting that adsorption between Cd(II) and VNC-1 was an exothermic process. The decrease in percentage may be due to desorption caused by an increase in the available thermal energy. At the high temperature higher mobility of the adsorbate is induced causing desorbed. This result shows that the nature of the adsorption processes is mainly due to the decrease in surface activity that has observed a similar result. Therefore, the optimum temperature at 33±2^{0}C is used for further experiments [31].

Table: 7 Effect of Temperature on removal, % and amount adsorbed, mg/g of Cd(II)

S.NO	Temperature of the Cd(II) mg/dm^3	Removal of Cd(II) %	q mg/g amount adsorbed
1	35	61.11	30.91
2	40	58.76	30.06
3	45	53.26	27.54
4	50	50.55	25.85
5	55	47.77	24.16

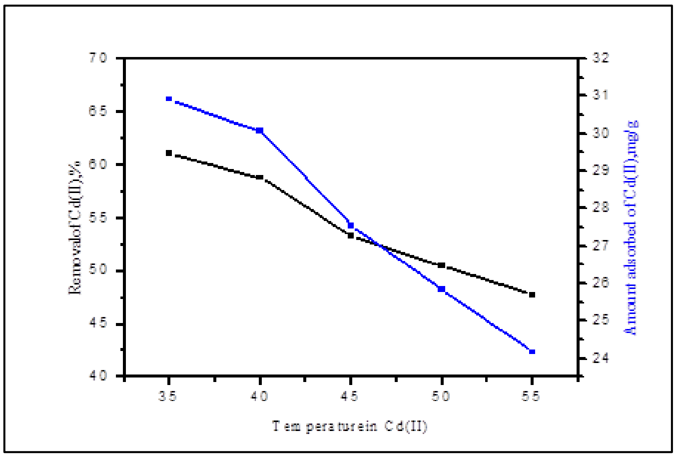

Figure-9 Effect of temperature on removal of Cd(II) from aqueous solution Conditions: Cd(II) =100mg/L; adsorbent dose=200mg; Size of adsorbent=0-53µ; pH=6

CONCLUSION

The present study shows that activated carbon prepared from chemically modified VNC-1 found to be an effective adsorbent for the removal of lead from aqueous solution. The adsorption process is a function of the concentration of adsorbent, pH, temperature and the size of the adsorbent. The maximum equilibrium was achieved practically in 180min further increment there is no significant increase in adsorption. The FTIR analysis of VNC-1 showed that different functional groups are involved in the adsorption of the Cd(II) ions and there is no appearance of any new functional group after adsorption of lead prove to adsorption occur through physically. The results may be very useful for designing an economically cheap treatment process for the removal of Cd(II) from Cd(II) containing wastewater from chemical industries.

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