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Studies on the Use of Carbon Waste Generated from Fertiliser Plant in Waste Water Treatment

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Abstract: Carbon waste generated from fertiliser plant has been used for adsorption studies for the removal of chromium, zinc and nickel and COD from industrial effluent from phenol formaldehyde plant, polyester plant, sugar plant. Removal to the extent of 91.40, 86.8, 93.8 percent was achieved at the initial concentration of 10 mg/l for Cr(VI), Ni(II) and Zn(II) respectively using carbon waste as adsorbent. Removal of these metals were found to be in order of Zn(II)>Cr(VI)> Ni(II). In a multi cationic solution containing these three metals, Cr(VI) adsorbed preferentially over Ni(II) and Zn(II). COD removal of 67.51%, and 86.4 % was obtained in case of polyester and sugar plant effluent respectively. In case of phenol formaldehyde resin COD removal to the extent of 65.00 % was obtained for the initial COD concentration of 1000mg/l.

Keywords: Carbon waste, carbon slurry, heavy metals, COD, polyester, surface area.

Introduction

Fertilizer industry is playing important role in meeting the one of the three basic needs of mankind and is responsible for green revolution all over the world. A number of nitrogenous fertilizer units use partial oxidation of naphtha, fuel oils and other heavier hydrocarbon feedstocks for the production of synthesis gas. During manufacture of ammonia in fertliser plants, carbon waste is produced as a byproduct during partial oxidation of hydrocarbons in the form of soot particles along with gaseous products such as CO_2, CO and hydrogen. Carbon waste is recovered by water scrubbing to get carbon waste in the form of slurry. This carbon waste is of no use to fertilizer industry and poses disposal problem. It is very rich in carbon content. Hence its usage should be explored.

Due to increasing population and large scale industrialisation water pollution problem has become an important issues during recent because of presence of large number of refractory organics and heavy metals which are not removed by conventional treatment processes. In order to meet the stringent regulatory parameters it has become essential to go for tertiary treatment processes for safe disposal. Adsorption is as a unit operation has been used by many researchers for the removal of various non-biodegradable materials from wastewater. Although activated carbon has many attractive properties like high surface area (300-1500 m^2/gm), high adsorption capacity for a large number of organic compounds, heavy metals, colour etc., its high cost and 10-15% loss in regeneration acts as major deterrents in its utilization as an adsorbent in the developing countries. Recently, low cost materials like coal fly ash, bottom ash, bagasse fly ash, peat, wood, sunflower stalks, peat mass, modified coal, bark, saw dust, coconut shell char for removal of refractory organics, heavy metal, colour, dyes, etc. have received considerable attention for use as adsorbents [1-11] A critical review on the subject has been presented by Mall et al. [10] and Bailey et al.[11].

The aim of the present investigation is to explore the possibility of utilizing carbon waste (CW) obtained from the ammonia plant for the removal of some of the heavy metals like Cr(VI), Ni(II) and Zn(II) which are commonly present in fertilizer plant waste water, and COD from waste waters generated in the phenol formaldehyde resin plant, polyester plant and sugar mill.

Materials & Method

Carbon waste was collected from the National Fertilizer Limited, Panipat(Haryana), India. Synthetic waste waters containing heavy metals ions like Cr(VI), Ni(II) and Zn(II) were prepared from K_2CrO_4 and chlorides of Ni and Zn (AR grade), respectively in the concentration range from 5 mg/l to 50 mg/l. Waste water samples from phenol formaldehyde resin plant, polyester plant and sugar mill were also collected for COD removal studies.

Proximate analysis and chemical analysis of the carbon waste (CW) were performed using standard procedure. Bulk density of the CW was determined using MAC bulk density meter. Particle size analysis was done using Malvern particle size analyser. X-Ray diffraction(XRD)analysis have been carried out using Phillips Diffraction Unit (Model PW 1140/90), using copper target with nickel as filter media , and K radiation maintained at 1.542 A°. Goniometer and chart speed were maintained at 1° min^{-1} and 1 cm min^{-1} respectively. Scanning Electron Microscopy (SEM) was carried out by using LEO 435 VP Scanning electron microscope. BET surface area, pore volume distribution and pore diameter of CW were determined using Flow Sorb 2300 Surface Area Analyser. The determination of concentration of heavy metals in the water sample were carried out using GBC Avanta Atomic Absorption Spectrometer (AAS) using acetylene-air flame for the aspiration of samples.

Batch experiments were carried out to study the effect of important parameters like adsorbent dose, initial concentration, contact time, adsorption isotherms and adsorption kinetics. For each experimental run, known volume of synthetic water samples with known concentration of Cr(VI), Ni(II) and Zn(II) and known amount of CW were mixed and agitated in a temperature-controlled shaking water bath at a constant speed of 145 revolutions per minutes at 30 ± 1°C. Water samples were withdrawn at appropriate time intervals, filtered and analysed for residual concentrations of Cr(VI), Ni(II) and Zn(II) using AAS. Adsorption studies for multi-cationic solution containing all the three metal ions were also carried out. Batch experiments were performed to study the removal of COD from various industrial waste waters using CW as the adsorbent. In all the batch studies 20 kg of carbon waste per cubic meter of wastewater was used.

Result and Discussion

Characterisation of Industrial Wastes: Detailed characteristics of the waste waters collected from phenol formaldehyde resin plant, polyester plant and sugar mill are given in Table 1.

Table 1 : Characterization of Different Industrial Waste Waters

Sr. No.	Characteristic	Polyester Waste Water		Phenolic Waste Water	Sugar Industry Waste
		Untreated	Treated		
1	pH	7.1	7.5	5.45	5.08
2	Total solids (mg/l)	800	520	-	1430
3	Suspended solids (mg/l)	45	30	-	1130
4	Dissolved solids (mg/l)	765	490	-	100
5	Turbidity (NTU)	-	-	29.2	166
6	DO (mg/l)	1.6	4.8	0.25	2.1
7	COD (mg/l)	440	147	184000	308
8	BOD_5 (mg/l)	220	40	12985	255
9	Chlorides (mg/l)	-	-	2.5	-
10	Phenols (ppm)	-	-	5000	-

Characterisation of Adsorbents: Adsorbent characteristics such as bulk density, surface area, pore volume, average pore diameter, average particle size are given in Table 2. Particle size distribution is given in Fig.1. XRD and SEM analysis are presented in Figs. 2 and 3 respectively. The SEM of CW shows very fine particle size of the order of micrometer or less. Major components identified from the XRD of the carbon waste are SiO_2 and $CaSiO_3$. The other peak is thought to be observed due to the presence of Al_2O_3 and Fe_2O_3. In IR spectra of carbon waste (Fig. 4), different bands were observed at 470(w), 500(w) 1000-2000(s), 2360(m), 3400(s), 3500(s), 3800(s), 3900(s)cm^{-1}. These data indicate the possibility of SiO_2, Al_2O_3, CaO, MgO in carbon waste. However, it was difficult to specify the presence of individual compound based on the spectra. Surface area of carbon waste was found to be 357 m^2/g.

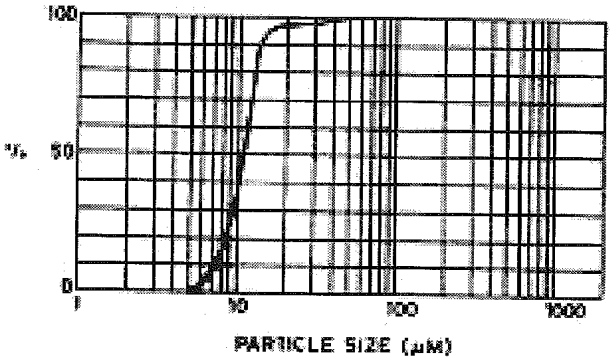

Fig. 1 Particle size distribution

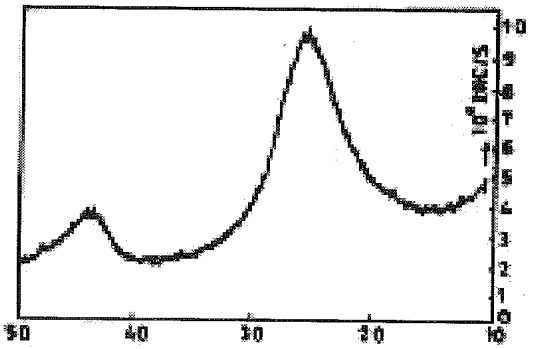

Fig. 2 X-ray diffraction pattern

Fig. 3 Scanning electron micrograph of carbon waste

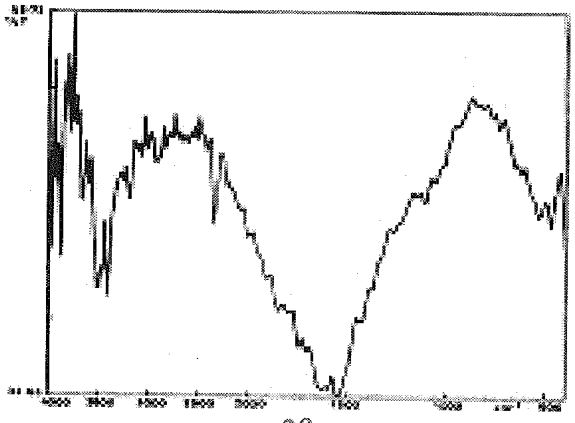

Fig. 4 IR spectra of carbon waste

Batch Adsorption Studies for Removal of Heavy metals

Effect of Adsorbent Dose: The effect of CW dose on the removal of Cr(VI) is shown in Fig.5. It can be seen from the figure that the percentage removal increases up to a maximum and there after it remains almost constant. For larger concentration of adsorbent, the adsorbate molecules have to travel considerable distance in order to reach large number of active sites. Therefore, percent removal does not show an

improvement with further increase in adsorbent dose. Similar results were also obtained for other heavy metals.

Table 2 : Proximate and Chemical Analysis of Adsorbents

Adsorbent	Surface Moisture (%)	Inherent Moisture (%)	Ash %	Volatile Matter (%)	Fixed Carbon (%)	Bulk Density (kg/m^3)
Carbon Waste	10.74	4.85	5.2	13.33	76.62	308.03

BET Surface Area: (m^2/g) 357.32; Pore Volume: (cm^3/g) 0.579; Avg. Pore Diameter: (Å) 64.83; Avg particle size:10μ; Calorific Value:(kJ/kg) 22279.8

Adsorbent	Loss on ignition (%)	Insoluble residue (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)
Carbon Waste	-	90.3	79.13	9.56	4.22	2.67	2.5

Effect of contact time and initial concentration: Fig. 6, 7 and 8 show the effect of contact time on the removal of Cr(VI), Ni(II) and Zn(II), respectively from the synthetic wastewater of known concentrations. It is found that the rate of removal is very rapid during initial 30-45 minutes and, thereafter, the rate decreases and no significant change is observed after 300 minutes. This can be explained on the basis of the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after some time, the remaining vacant surface sites are difficult to occupy due to repulsive forces between the solute molecules of the solid and the bulk phase. Percent removal of adsorbate increases with decrease in its initial concentration while uptake of heavy metals increases with increase in concentration (Figs. 6, 7 and 8).

Kinetics of adsorption: The kinetics of adsorption is generally determined by using the Lagergren Equation [5,9]

$$\log(q_e - q) = \log q_e - \frac{k}{2.3}t$$

where q_e = amount of adsorbate adsorbed at equilibrium, mg/g; q = amount of adsorbate adsorbed at time t, mg/g; k = adsorption rate constant, min^{-1}, t = time, min. The plot of log $(q_e - q)$ against time is shown in Fig. 9 for the removal of Cr(VI), Ni(II) and Zn(II). The straight line plot shows the validity of Lagergren equation. Table 3 gives the value of adsorption rate constant, K.

Intraparticle diffusion study: A functional relationship commonly used to describe the intraparticle transport is the plot between mass of solute adsorbed per unit mass of adsorbent (q) and square root of contact time ($t^{0.5}$), the Weber-Morris plot. The linear nature of the plot shows that the controlling mechanism for adsorption is intraparticle diffusion [6]. These plots for Cr(VI), Ni(II) and Zn(II) are shown in Fig. 10. The

plot of q_e versus $t^{0.5}$ is found to be linear for a wide range of contact time for carbon waste and the solution of these heavy metals. The values of intraparticle diffusion rate parameters are given in Table 3.

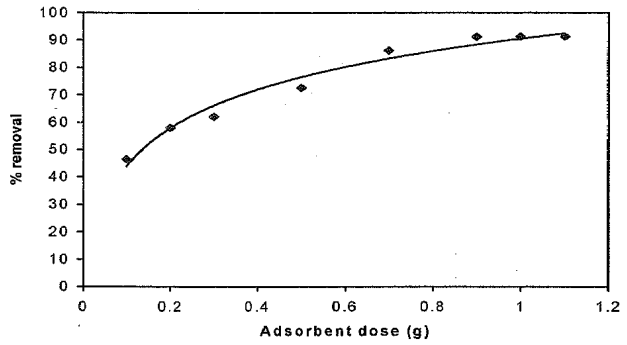

Fig. 5 : Effect of adsorbent dose on removal of Cr(VI)

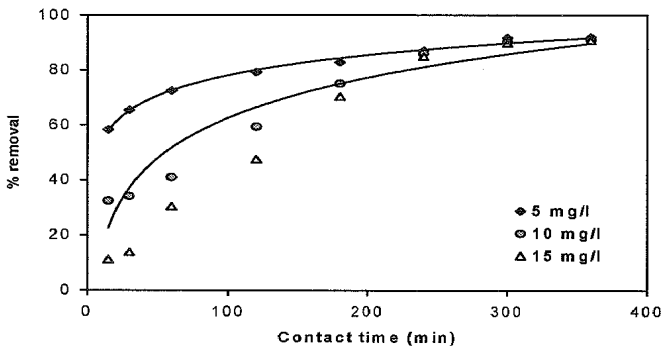

Fig. 6 : Effect of contact time on removal of Cr(VI)

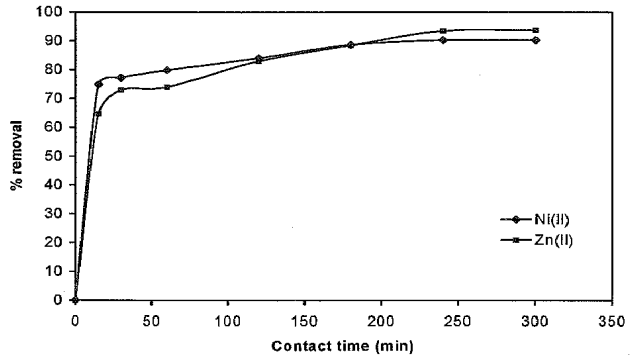

Fig. 7 : Effect of contact time

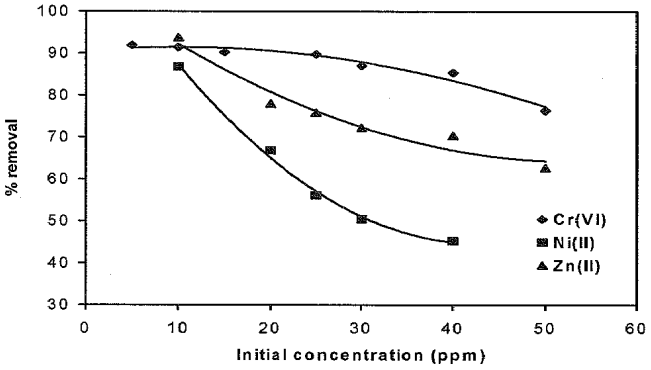

Fig. 8 : Effect of initial concentration

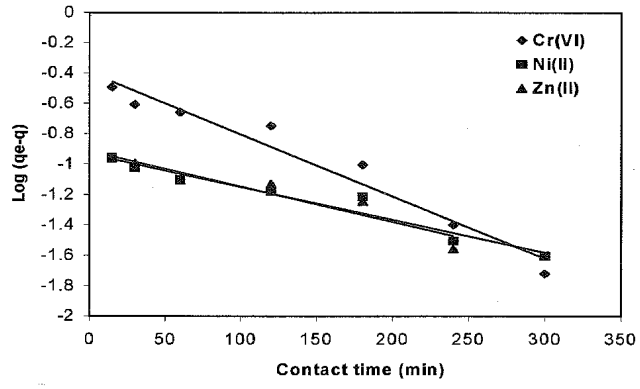

Fig. 9 : Lagergren plot

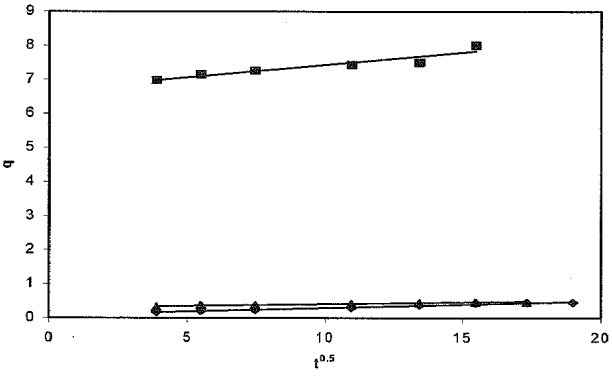

Fig. 10: Weber-Morris Plot

Adsorption isotherm equations: Freundlich and Langmuir isotherm equations have been used to describe the equilibrium adsorption of heavy metals from their synthetic solutions. The Freundlich isotherm is represented by the equation ;

$$q_e = K_F C_e^{1/n} \quad \text{or} \quad \log q_e = \log K_F + \frac{1}{n}\log C_e$$

The Langmuir isotherm is represented by the equation

$$q_e = \frac{q_m K_A C_e}{1 + K_A C_e} \text{ or } \qquad \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_A q_m}\left(\frac{1}{C_e}\right)$$

Fig.11 gives the plot of log q_e against log C_e. for Cr(VI), Ni(II) and Zn(II). Similarly Fig.12 give the plot of $1/q_e$ against $1/C_e$ for Cr(VI), Ni(II) and Zn(II). Straight linear relationships of experimental data show the validity of these isotherms. The values of parameters for Freundlich and Langmuir isotherms are given in Table 4.

Table 3 : Adsorption rate constant, K and Intraparticle Diffusion Rate Parameter, k for Removal of Cr (vi), Ni (ii) and Zn (ii) from Aqueous Solutions by Carbon waste.

Sr. No.	Adsorbate	Lagergren constant, K (min^{-1})	Intraparticle diffusion rate parameter, k ($mg\ g^{-1}\ min^{-0.5}$)
1	Chromium (VI)	0.2056	0.0208
2	Nickel (II)	0.8214	0.0739
3	Zinc(II)	0.1127	0.0108

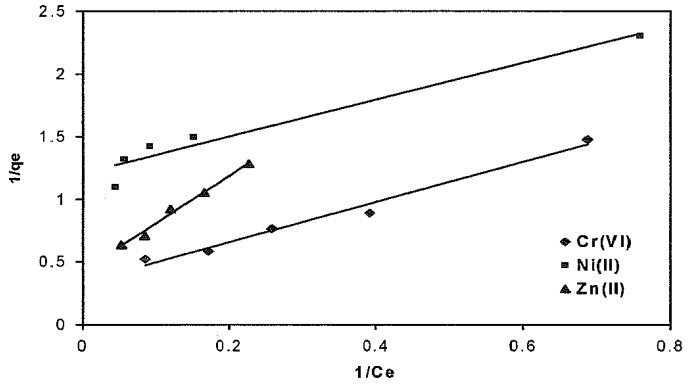

Fig. 11 : Langmuir isotherm

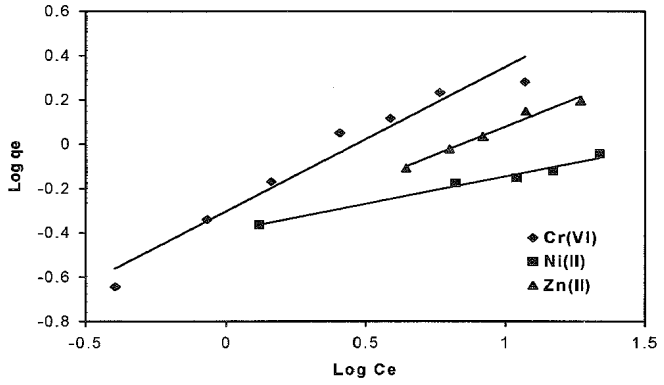

Fig. 12 : Freundlich isotherm

The value of separation factor or equilibrium constant R_L [10] which is defined as $R_L = 1/(1 + bC_i)$ (where C_i is initial concentration and b is Langmuir constant) indicates the nature of adsorption as $R_L > 1$ Unfavourable; $R_L = 1$; Linear; $0 < R_L < 1$ Favourable; $R_L = 0$ Irreversible. The values of R_L for Cr(VI), Ni(II) and Zn(II) are also given in Table 4. The value of R_L is found to be less than 1 showing favourable

Table 4 : Isotherm Parameters and Separation Factor R_l for the Removal of Heavy Metal by Carbon Waste

Adsorbent	Adsorbate	Freundlich Isotherm		Langmuir Isotherm		R_L
		K_F,$(mg/l)^{-1/n}$	n	q_m(mg/g)	$K_A(mg^{-1})$	
Carbon waste	Cr(VI)	0.7825	1.7191	3.2573	0.2056	0.0101
	Ni(II)	0.4045	4.0420	0.8288	0.8214	0.0386
	Zn(II)	0.3756	1.9829	2.3392	0.1127	0.0140

adsorption of Cr(VI), Ni(II) and Zn(II) on carbon waste. The values of 1/n for Freundlich isotherms were also found to be less than 1, further reinforcing the conclusion of favourable adsorption [11].

Competitive adsorption for multi-cationic solution: Removal of Cr(VI), Ni(II) and Zn(II) in competitive environment was studied. Percent removal of Cr(VI), Ni(II) and Zn(II) was about 88%, 42% and 60% respectively. From the results we can see that Cr(VI) is readily adsorbed in comparison of Ni(II) and Zn(II).

Batch Study for the Removal of COD from Industrial Wastewater

A typical industrial wastewater from phenol formaldehyde resin plant was taken and diluted to form solutions of different initial COD. Fig13 show the plot of % COD removal versus initial concentration time. Percent removal was found to increase with decrease in initial concentration. Removal to the extent of 65%was achieved at the initial concentration of 1000 mg/l. Equilibrium data shows the applicability of Langmuir Isotherms in Fig.14. The values of Langmuir adsorption isotherm parameters are given in Table 5.Treated and untreated combined waste from polyester plant was treated in a constant temperature incubator shaker with carbon waste. About 67% and 81% removal was observed for treated and untreated wastewater respectively. It also shows that percentage removal is high in case of low concentration effluents. Combined wastewater from a sugar mill was also treated with carbon waste and about 86.4% COD removal was observed. Complete removal of color was also seen in this case. Table 6 shows the percentage COD removal from phenol formaldehyde resin plant, polyester plant and, sugar plant.

Table 5: Langumir Isotherm Parameter the Removal of COD by Carbon Waste from Phenol Formaldehyde Resin Plant

Adsorbent	Langmuir Isotherm	
	q_m (mg/g)	K_A(mg^{-1})
Carbon waste	0.332	319.68

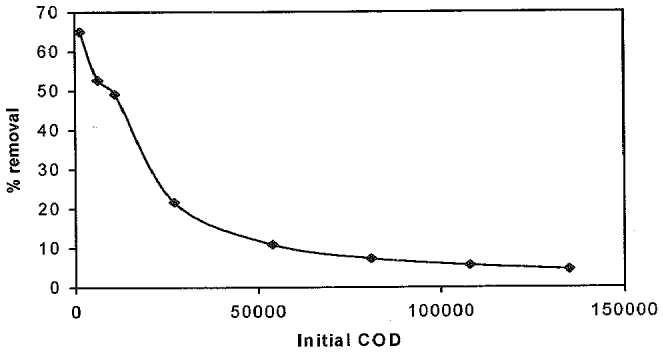

Fig. 13 : Effect of initial concentration (COD) on removal of COD from phenol formaldehyde resin plant waste

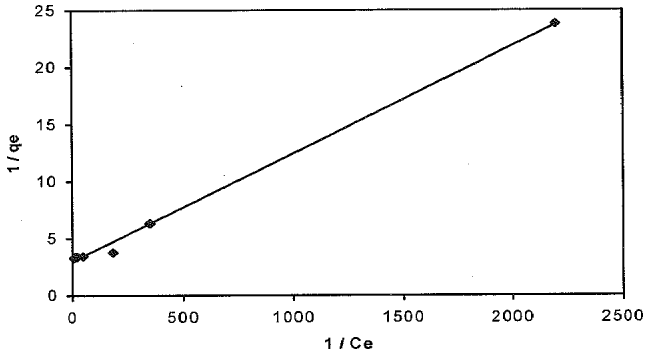

Fig. 14 : Langumir isotherm for the removal of COD from phenol formaldehyde resin plant waste

Table 6: COD Removal From Phenol Formaldehyde Resin Plant, Polyester plant and & Sugar Mill Waste Using Carbon Waste

Sample	% Reduction
Phenol formaldehyde plant (initial conc. 1000mg/l)	60
Polyester plant untreated waste	67
Polyester plant treated waste	81
Sugar industry sample	86.4

Conclusions

Based on the present investigation it may be concluded that carbon waste has high potential for the removal of heavy metals and COD. from industrial effluent. Carbon waste has surface area quite comparable to activated carbon. As carbon waste is available as waste its utilisation will be economically viable in the waste water treatment. Carbon waste can be regenerated or can be used as fir briquettes as it has very high carbon content and calorific value.

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