RESEARCH ARTICLE

ADSORPTION STUDIES OF PB (II) FROM AQUEOUS SOLUTION BY USING MODIFIED DATE PALM TRUNK.

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Manuscript Info	*Abstract*
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Ethylenediamine modified date palm trunk an attractive approach for improvement of lead (II) uptake from aqueous solutions. Factors influencing Pb(II) adsorption onto MDPT such as initial Pb (II) concentration, pH, contact time, and adsorbent dosage were investigated. The adsorption equilibrium was established within 120 min. Before and after adsorption, MDPT was characterized by Fourier transform infrared spectroscopy (FTIR). The results showed that the pseudo-second order model fits the experimental data very well. The equilibrium data have been analysed using Langmuir and Freundlich isotherm models. The recovery of Pb(II) adsorbed on MDPT was found 98.5% using 0.2 M HCl. Desorption experiments showed the feasibility of the regeneration of MDPT.

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Introduction:-

A large variety of heavy metals is discharged into the environment and constitutes the most significant environmental pollutants found in wastewater. Long-term exposure to those solvated metal ions and consequently the effects on human health and natural ecosystems are critical issues. Lead is considered severe toxic and more hazardous to the environment and organisms compared to "the big three" of heavy metals (others are Cd and Hg) [1]. Lead is generated into the environment from various industrial effluents such as metal electroplating, mining, extractive metallurgy and battery manufacture [2]. Biosorption is a promising method for removal of heavy metals from waste water because of its advantage of low cost and good adsorption potential. Adsorption is the most preferred method for removal of heavy metals from aqueous solutions due to its simplicity and its high effectiveness [3-5].

In recent years, many agro wastes, including sawdust [6], carrot residue [7], sugar beet pulp [8], tree fern [9], rice husk [10], papaya seed carbon [11], eucalyptus bark [12] and date palm trunk [13], had been used to adsorb heavy metals from aqueous solution. The agricultural wastes being abundantly available with low cost mainly comprise of cellulose which is a natural biopolymer with sorption property. For improving the adsorption capacities of agro wastes, various chemical modifications have been reported [14, 15].

The purpose of this study is to utilize date palm trunk (cellulosic agro wastes) after its chemical modification as a potential adsorbent for treatment of wastewater containing Pb(II). The values of well-known kinetics and isotherms

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studies have been performed to elucidate the equilibrium adsorption behavior of Pb(II) onto the adsorbent. The effect of contact time, pH, concentration and dosage on the adsorption capacity has been investigated.
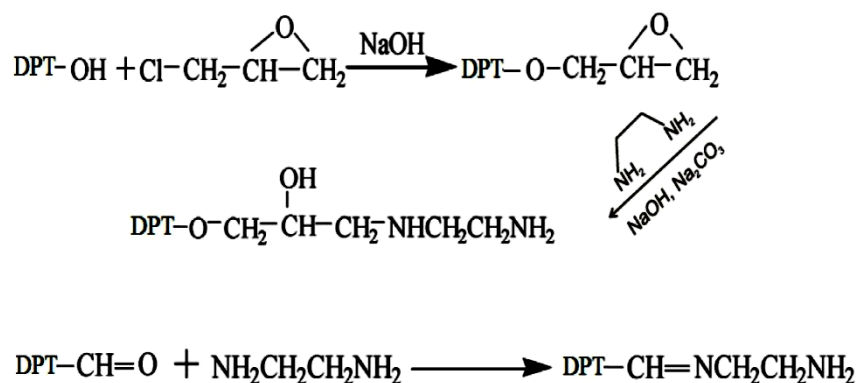
Materials and Method:-
Chemicals and Instrumentation:-
All the chemicals used were of analytical reagent grade. Stock solution of 1000 mg/L of Pb(II) was prepared by dissolving 1.6 g of $Pb(NO_3)$ in distilled water and making the volume up to 1000 mL in a volumetric flask. The pH of each of the working solutions was adjusted by using 0.1M HCl or 0.1 M NaOH. Systronic digital pH meter was used for pH measurements. FTIR spectrometer (Perkin Elmer System- 1600) was used for IR spectral studies. UV-visible double beam spectrophotometer (Systronics UV-Vis-2203) was used for determination of Pb(II) concentration using 1,5- diphenyl thiocarbazone in aqueous miceller solution. An electrically thermostatic rotary shaker (IEC-56, India) was used for agitating the samples.

Preparation of MDPT:-
Date palm trunk (DPT) was obtained from rural areas around Kanpur (India), cut into a length of approximately 1 cm, washed thoroughly with demineralized water (DMW) to remove water soluble materials, dried overnight at 100 $\pm$ 2°C in a hot air oven, and allowed to cool down to room temperature. It was ground and sieved to obtain an average particle size of 75 μm. DPT powder (10 g) was treated with 80 mL of NaOH solution (1.25 mol/L) and epichlorohydrin (30 mL) at 40 ^{0}C for 1 h. Then mixture was filtered, rinsed with water, oven-dried and stored in a desiccator. During the treatment, the hydroxyl groups of DPT reacted with epichlorohydrin. Modified date palm trunk was prepared by adding ethylenediamine (10 mL), water (100 mL) and Na_2CO_3 (1 g) to the epichlorohydrin treated DPT. The mixture was stirred using magnetic stirrer at 60 ^{0}C for 2 h, MDPT was filtered, washed with water, dried and stored in desiccator. The following chemical reactions occurred during the modification.

Batch Adsorption Studies:-
For adsorption studies, 0.1g MDPT was added to a series of Erlemeyer flasks filled with 20 mL lead (II) solutions (12.5-100 mg/L) and pH (1-6) sealed with parafilm and then shaken at 30^0C till equilibrium was reached. The sample solution was filtered using Whatman No. 4 filter paper and the filterate was analyzed for Pb(II) by spectrophotometric method using 1, 5-diphenyl thiocarbozone in aqueous miceller solution [16]. The adsorption capacity (q_e) and percentage removal of Pb(II) from aqueous solution is calculated by following equations,

$$q_e = \left(\frac{C_i - C_e}{M} \right) V \qquad (1)$$

where, C_o and C_e (mg/L) are the initial and equilibrium concentrations of Pb(II) ions in solution; V is the volume (L) of the solution and M is the weight (g) of dry adsorbent.

$$\% Removal = \left(\frac{C_i - C_e}{C_i} \right) 100 \qquad (2)$$

Result and Discussion:-

FT-IR analysis:-

FTIR spectra (fig. 1) shows MDPT and Pb(II) loaded MDPT. The broad peak around 3410 cm^{-1} in MDPT is attributed to –NH stretching vibration. This absorption band is shifted towards lower wave number (3381 cm^{-1}) in case of with Pb(II) adsorbed MDPT. This suggests the formation of complex between Pb(II) ions and N-atoms (The characteristics band at 1056 cm-^{1} corresponding to C-O-C stretching is observed in both spectra).
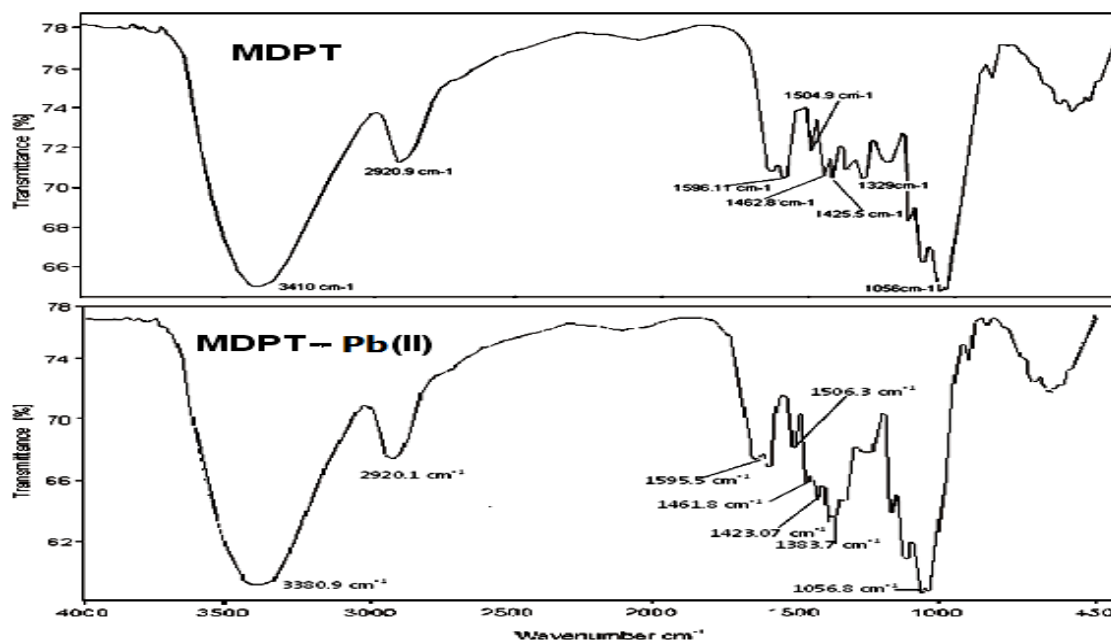

Figure 1:- FTIR spectra of MDPT and MDPT-Pb(II) loaded.

Effect of pH:-

The pH of solution is an important controlling parameter in the adsorption process. Since, pH influences the solution chemistry of the heavy metals (i.e. hydrolysis, complexation, redox reactions and precipitation), and the solution chemistry of the heavy metals also strongly influences the speciation and the adsorption availability of the heavy metals. The binding of metal ions by surface functional group (–NH) is strongly pH dependent [17]**.** Fig. 2 shows that Pb(II) removal is minimum at pH 1 and increases with the increase in pH. Removal of Pb(II) was found maximum at pH~5.
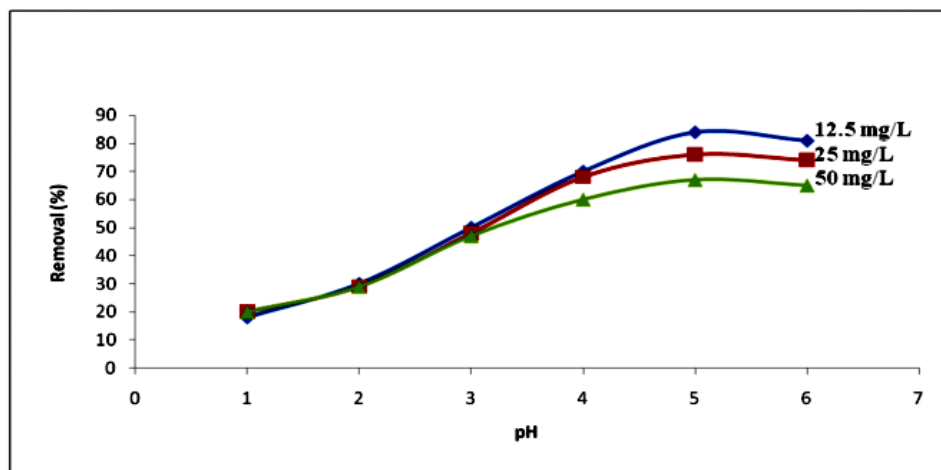

Figure 2:- Effect of pH of solution on the removal of lead(II).

Effect of Adsorbent Dose:-
Effects of dosage on the removal of Pb(II) ions is shown in Fig. 3. It was observed that the removal of lead(II) increases rapidly with increasing dosage from 0.0 to 0.5 g/L. After certain adsorbent dosage the removal efficiency does not increase significantly and reached the maximum at dosage of 0.6 g. The removal of Pb(II) for concentrations 12.5, 25 and 50 mg/L using 0.6 g/L MDPT was 98.2%, 95% and 90%, respectively. On increasing adsorbent dosage, more surface area is available for the adsorption due to an increase in active sites on the adsorbent and its availability for adsorption.
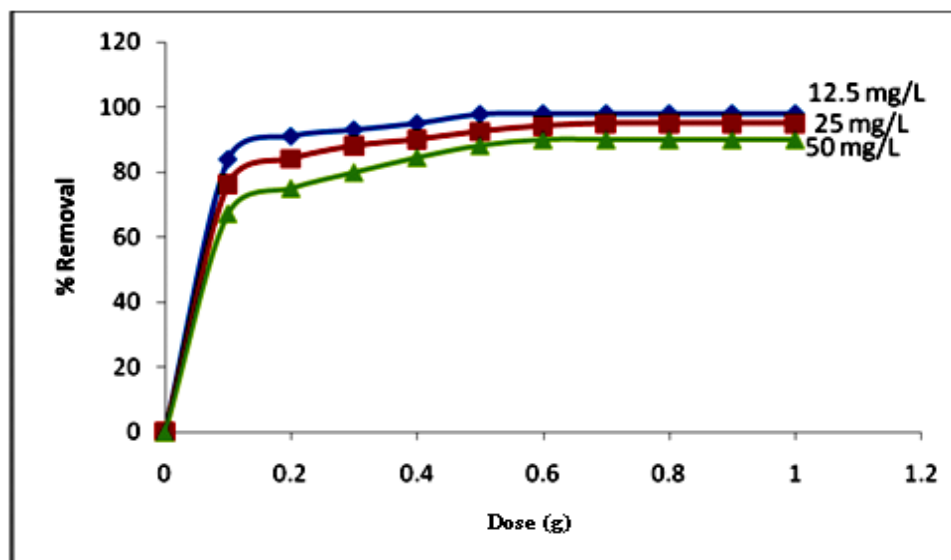

Figure 3:- Effect of adsorbent dose on the removal of lead (II).

Effect of Contact Time:-
Figure 4 shows that with increase in contact time removal increases rapidly during the first 15 min, and then it was moderate up to 30 min and there after remained constant. This behavior may be due to saturation of the available adsorption sites present on MDPT. At the initial stage, the removal efficiency was rapid due to abundant availability of active binding sites on the biomass and with gradual occupancy of these sites; sorption became less efficient in the later stages**.** The equilibrium is established with in 120 min.
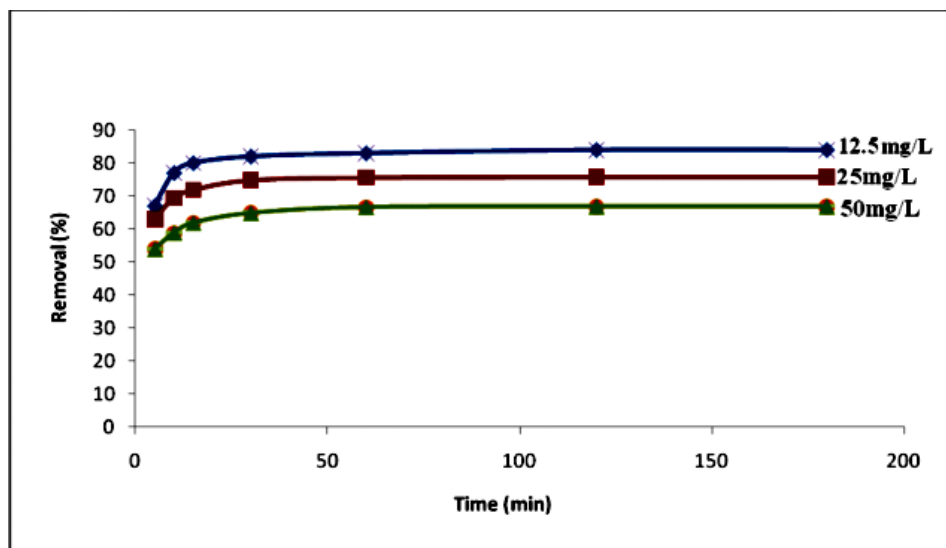

Figure 4:- Effect of contact time on the removal of lead(II).

Adsorption Kinetics:-

In order to evaluate the kinetic mechanism that controls the adsorption process, the pseudo-first-order and pseudo-second-order models were used. The pseudo first-order equation [18] is generally expressed as follows:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303) \, t \qquad (3)$$

where k_1 (min^{-1}) is the pseudo-first-order adsorption rate constant, q_t (mg/g) denotes the amount of sorption at time t (min), and q_e (mg/g) is the amount of sorption at equilibrium. The pseudo-second-order equation [19], based on adsorption capacity at equilibrium, can be expressed as:

$$t / q_t = 1 / k_2 q_e^2 + (1/ q_e) \, t \qquad (4)$$

where k_2 (g/mg min) is the rate constant of the pseudo-second-order equation, q_e (mg/g) is the maximum adsorption capacity, and q_t (mg/g) is the amount of adsorption at time t (min).

The values of pseudo-first order rate constants, k_1 and q_e were calculated from the slopes and the intercepts of the plots of log (q_e-q_t) versus time (Fig. 5). The k_1 values, the correlation coefficient R^2, and theoretical and experimental equilibrium adsorption capacity q_e are given in Table 1. The R^2 values in Table 1 suggest that adsorption of Pb(II) onto MDPT does not follow pseudo-first-order kinetics. In addition the theoretical and experimental equilibrium adsorption capacities, q_e obtained from these plots varied widely. This confirms that the pseudo-first-order model was not appropriate for describing the adsorption kinetics of Pb(II) onto MDPT. On the contrary, the kinetics data showed excellent fit to the pseudo-second-order equation. The plot of t/q_t against t at different concentrations is shown in Fig. 6. The pseudo-second-order rate constant k_2, the calculated q_e values, and the corresponding R^2 values are given in Table 1. From Table 1, it is evident that the calculated q_e values agree with experimental q_e values well, and also the correlation coefficients for the pseudo-second order kinetics plots at all the studied concentrations are higher ($R > 0.99$).

It can be concluded that the adsorption proceeds via pseudo-second-order mechanism rather than a pseudo first-order mechanism.

Table 1:- Adsorption kinetics for removal of Pb(II) onto MDPT

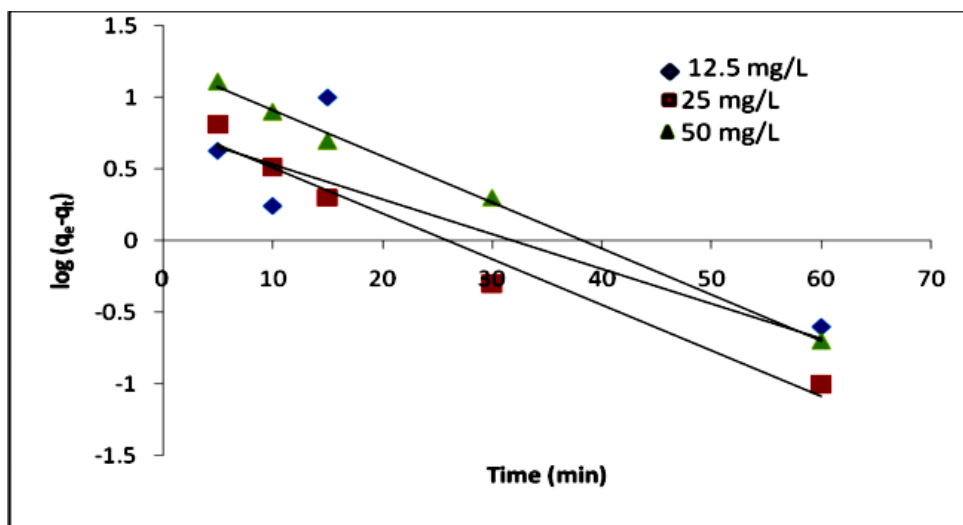| Conc. (mg/L)	$q_{e \cdot exp.}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	$q_{e \, (cal)}$ (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e \, (cal)}$ (mg/g)	R^2
12.5	21.0	0.024	5.97	0.875	0.0448	21.27	0.999
25	38.0	0.032	6.82	0.971	0.0242	38.46	0.999
50	67.0	0.032	9.35	0.997	0.0098	68.41	0.999

Figure 5:- Pseudo-first-order kinetic model for Pb(II) adsorption onto MDPT.
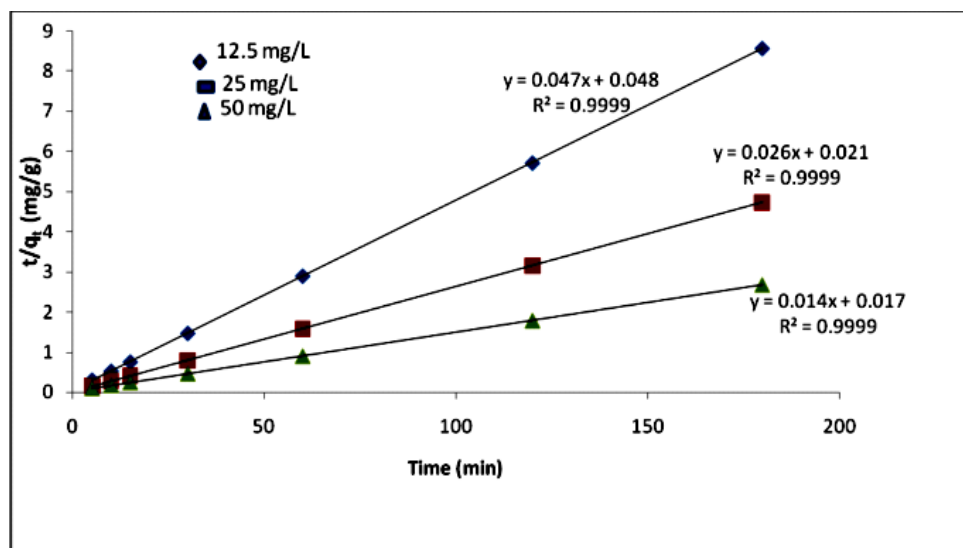

Figure 6:- Pseudo-second-order kinetic model for Pb(II) adsorption onto MDPT.

Adsorption Isotherms:-

Langmuir adsorption isotherm [20] was applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites. The following Langmuir sorption isotherm equation can be used:

$$C_e / q_e = 1 / b\, K_L + C_e / b \tag{5}$$

where q_e is the amount of Pb(II) adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of the Pb(II) in solution (mg/L), b is the maximum Pb(II) uptake (mg/g), K_L is the Langmuir biosorption constant (L/ mg) relating the free energy of biosorption. The essential characteristics of the Langmuir isotherm can be conveniently expressed in terms of a dimensionless term R_L (a constant separation factor or equilibrium parameter for a given isotherm) and is defined as:

$$R_L = 1 / (1 + K_L C_o) \tag{6}$$

where C_0 is the initial concentration of Pb(II) and R_L value indicates the type of the isotherm.

Freundlich adsorption isotherm [21] is an empirical relationship established upon adsorption onto a heterogeneous surface on the assumption that different sites with several adsorption energies are involved, and is given below:

$$\ln q_e = \ln K_F + 1/n \log C_e \tag{7}$$

where q_e and C_e are the equilibrium concentrations of Pb(II) in the adsorbed and liquid phases in mg/g and mg/L, respectively. K_F and n are the Freundlich constants.

The correlation coefficients (R^2) obtained using Langmuir (Fig. 7) and Freundlich (Fig. 8) have been listed in Table 2. $R^2 > 0.99$ obtained with Langmuir model supports that the biosorption of Pb(II) onto MDPT followed the Langmuir model. According to Mckay et al. [22] R_L values between 0 and 1 indicate the isotherm favourable, and it is unfavourable if $R_L > 1$. The obtained R_L values (0.089-0.439) indicate that the adsorption of Pb(II) onto MDPT is favourable and attributed to chemical ion-exchange mechanism.

Table 2:- Langmuir and Freundlich parameters for the adsorption of Pb(II) onto the MDPT.

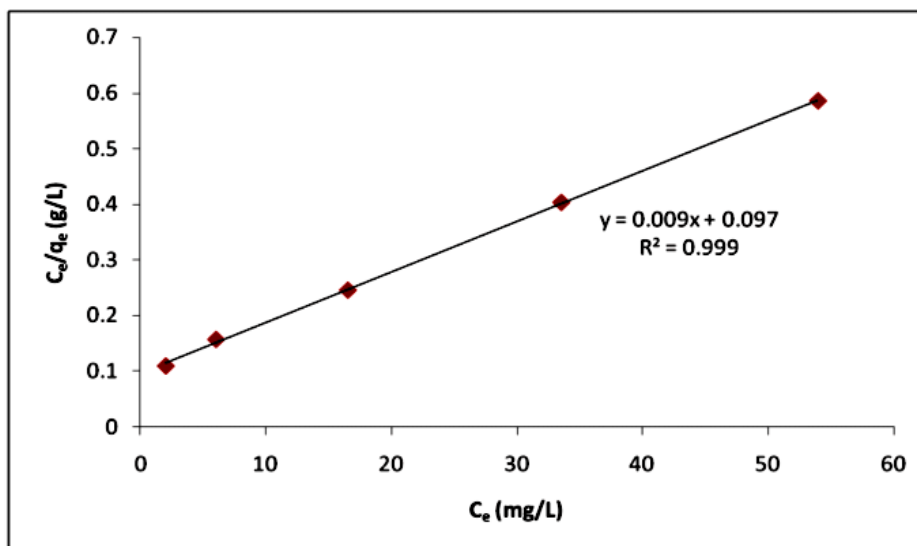| *Isotherm*	*Parameters*	*Values*
Langmuir	q_m (mg/g)	108.2
	b (L/mg)	0.101
	R^2	0.997
Freundlich	K_f (mg/g)	16.26
	n	2.17
	R^2	0.978

Figure 7:- Langmuir isotherm plot for Pb(II) adsorption onto MDPT.
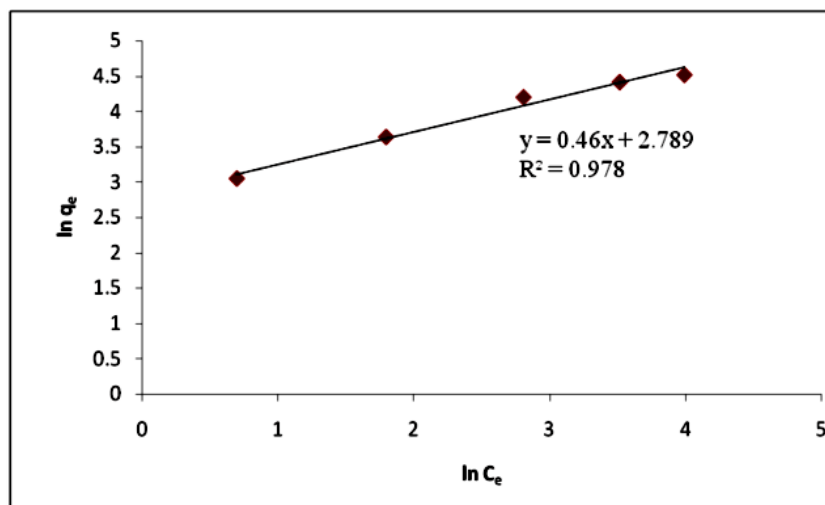

Figure 8:- Fruendlich plot for Pb(II) adsorption onto MDPT.

Desorption:-

Desorption studies were conducted in order to explore the feasibility of recovering both the metal ion and MDPT. MDPT (0.1g) was transferred into 20 mL of 0.01-0.2 M HCl solution in a conical flask, and shaken for 4 hours at room temperature (30 ± 1^0C).The rate of desorption increases with the increases in conc. of HCl upto 0.2 M and remains unchanged at higher conc. of HCl. The maximum percentage recovery of lead was 98.5% (Fig. 11). The results of desorption studies show that the most of Pb(II) ions on MDPT surface might be held through ion-exchange/ complexation type of binding. Therefore, recovery of the adsorbed lead(II) and repeated usability of MDPT is feasible as an adsorbent in the practical applications of treatment of industrial effluents containing Pb(II).
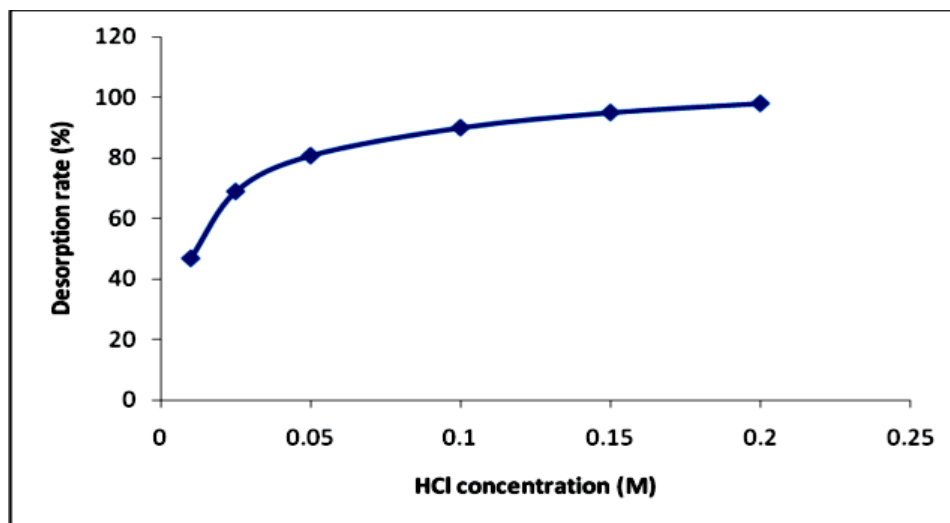

Figure 9:- Effect of HCl concentation on the desorption of Pb(II).

Conclusions:-

Adsorption of Pb(II) onto MDPT was studied. The adsorption was found greatly dependent on pH and contact time. The adsorption equilibrium was best described by the Langmuir isotherm model. The maximum adsorption for Pb(II) was found to be 108.2 mg/g at pH 5. The adsorption is followed by pseudo-second order kinetics, which shows the chemisorptions process. The adsorption capacity of MDPT is higher than many of the biosorbents reported earlier. The desorption percentage was 98.5% using 0.2 M HCl as an eluting reagent.

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