ADSORPTION OF Mn (II) FROM AQUEOUS SOLUTIONS USING PITHACELOBIUM DULCE CARBON

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ABSTRACT

Pithacelobium dulce carbon (PLDC) was found to have good sorption capacity for Mn (II) ion. Studies indicated that sorption of Mn (II) ion increases with increase in pH and a contact time of 50 minutes was found to be optimum. The effect of concentration shows that fruit shell can remove Mn (II) ion. With the increase in the concentration of substrate the sorption also increases. The presence of Fe^{+2} and F^- ions interfered with the adsorption of Mn (II) ion.

Keywords: PLDC, Adsorption, pH, Metal removal.

INTRODUCTION

The removal of metal ions like Mn (II) ion from aqueous solution is serious problem in many countries. Manganese is one of the most difficult elements to remove from surface waters [1, 2, 3]. Although dissolved Mn(II) ion is not known to be toxic, and even blocks the toxic effect of H^+ion[4].

It has undesirable effects on water use. These include training laundry and ceramic fixtures such as toilets where concentrations are greater than 0.05 mg/L[5]. Federal relations therefore control discharge limits. In drinking water sources, the secondary maximum contaminant level (SMCL) for Mn(II) ion must not exceed 0.05mg/L [6].

Many studies have been conducted on Mn(II) ion removal in the past, including those designed to evaluate chemical dynamics, experiment with packed columns of limestone, and evaluate passive treatment systems[7, 8, 9]. Microbial remediation efforts include designed wetlands, microbial bioreactors, and pellets of mixed microbial cultures etc[10, 11, 12, 13]. Prasenjit Mondal[14] reported that Mn can be removed by 41% by using GAC. Dinesh Mohan[15] reported that Mn is removed by using lignite upto 25.84%. M. M. Nassar[16] reported that removal of manganese ion by adsorption on palm fruit bunch and maize cobs was in the range of 79-50%. M.Saad[17] reported that manganese is removed from wastewater by using sulphurized activated carbon obtained from burnt date stones.

In the present water management study the author prepared some adsorbent materials from agricultural wastes and an attempt was given to remove water soluble Mn (II) ions by adsorption with prepared activated carbons.

EXPERIMENTAL

All the reagents used in the experiment were of analytical grade. A initial stock solution of Mn(II) ion was prepared by dissolving requisite manganese sulphates. A standard solution of Mn(II) ion were prepared by taking different aliquot from stock solution with subsequent dilution with distilled water.

Preparation of Adsorbent

Dried fruit shell of PLDC were carbonized in the electrical conventional heating reactor by two stages carbonization process in the range of 250-600 ^{0} C and 600 – 800 ^{o} C respectively. The materials were placed in closed stainless steel vessels by maintaining inert conditions and pyrolysis was carried out at $4O^oC$ for 30 Minutes followed by next stage to develop the pore size structure so that an accessible internal surface could be created.

The carbonized product was treated with acid (0.5 M HNO_3) for the removal of unwanted materials. The acid washed product was thoroughly washed with hot distilled water to remove acidity and chlorides. Indigenously prepared carbon thus produced was thermally activated at 120 ^{o} C for 1 hr in an air oven. The product was finally dried and sieved to get particular particle size i.e. 45μ.

Standard manganese solution preparation:

A stock solution of manganese solution used in this study was prepared by dissolving an accurate quantity of 1.000 g of manganese metal in 50 ml of 6N HNO_3 and dilute to 1000 ml. Other concentrations were prepared from this stock solution by dilution. Fresh dilutions were used for each experiment. The entire chemicals used were in analytical grade.

Apparatus

The apparatus used are

1. Atomic absorption spectrophotometer(ECIL AAS4103/AAS4127)
2. Elico-pH Meter
3. Remi shaker(2L)

Analytical method: manganese ion concentration of the solutions were determined by using an Atomic absorption spectrophotometer (ECIL AAS4103/AAS4127) with an air – acetylene flame oxidizing (lean, blue) and with light source of hallow cathode lamp. Deuterium back ground correction was used and the spectral slit width was 0.2 nm. The working current and wave length were 5.0 mA and 279.5 nm, respectively. The instrument response was periodically checked by using standard metal solutions.

Sensitivity: for the standard conditions described above, the sensitivity about 0.04 mg/ml Mn (II) ion for 1% absorption. A standard containing 1 mg/ml Mn(II) ion will typically give an absorbance reading of about 0.11 absorbance units (about 40 % absorption).

Linear working range: for the standard conditions described above the working range for Mn(II) ion is linear up to concentration of approximately 60 mg/L in aqueous solution.

RESULTS AND DISCUSSION

Effect of pH:

The effect of pH on adsorption of Mn(II) ion on PLDC is studied in the range 5.o to 9.0 pH and the results are summarized in Table 1 and Figure1. The percentage removal of Mn(II) ion increases with increase in the pH from 5.0 to 7.0 and it is almost constant up to pH 9.0 . From this study, it is observed that the change in pH is significant up to pH 7.0 and there is no considerable change after the pH 7.0.

Effect of adsorbate ion concentration:

The effect of adsorbate ion concentration is studied by taking 5,7,10,12,15,20,25 mg/L with an optimum pH value. The rate of Mn(II) ion adsorption on PLDC is achieved as presented in the Table 2 and Figure 2.The percentage removal decreased with increase of initial concentration of the Mn(II) ion. This may due to the lack of available active sites for the adsorption of high initial concentration of Mn(II) ion .

Effect of adsorbent dose:

The study of effect of dose of adsorbent is necessary and very useful to find out the optimum amount of carbon required for the removal of Mn(II) ion. The effect of adsorbent dose studies is observed from 1.00mg/L to 20.00 mg/L and is shown in Table 3 and in Figure 3. The equilibrium value of amount adsorbed (Qe) decreases with increase in dose. The percentage removal of metal ion was found to increase exponentially with the increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose of adsorbent, especially at higher doses. The relative increase in the extent of removal of Mn(II) ion is found to be insignificant after a dose 5g/L in the case of PLDC which is fixed as the optimum dose of adsorbent.

Effect of contact time:

In the adsorption system contact time place a vital role, irrespective of the other experimental parameters that affects the adsorption kinetics. The effect of contact time on the percent removal of Mn(II) ion was investigated at the optimum initial concentration of Mn(II) ion and the data are represented in Table 4 and Figure 4. It was found that the removal of metal ion increases with increase in contact time to some

extent. The removal of metal ion (in terms of metal adsorbed i.e.Qe) by the adsorbent (PLDC) increases, reaches maximum value and then decreases with the increase in contact time (may be due to desorption process)The relative increase in the extent of removal of metal ion (Qe) after 50 minutes of contact time is negligible and hence it is the optimum contact time.

Effect of common ions:

The presence of the common ions coexisting with manganese invariably implies competition for available adsorption sites. Mn(II) ion on the activated carbon some competition experiments were carried out to investigate if the considered metal ions are really adsorbed on different sites. Although some adsorption sites can only adsorb certain solutes and not all solutes compete for exactly the same sites, the presence of other solutes will reduce the adsorption of any given solute to some degree. Moreover, the adsorption of the other ions affects the recovery of Mn(II) ion directly. In potable water and in some industrial effluent waste water, the main cation is Fe^{2+} ions , the main anion is F^- .100 milliliters of 10mg/L solution as Mn(II) ion containing each of the above ions (50 or 100 mg/L) was shaken with 5 g PLDC at a pH 7.20. It was shown in Table 5 and the influence of Fe^{2+} on the adsorption of Mn(II) ion were rather significant since they compete for the active surface with manganese ions at this pH. In thesis present study results indicating that the concentrations of added elements decreases the adsorption efficiency of PLDC in manganese removal and also it reveals that the efficiency slightly decreases when Fe^{2+} ion concentration increases,. This also supports that there is a more competition between Mn(II) ion and Fe^{2+} ions into outer surface of the PLDC.

Regeneration and recycling studies:

Since Mn(II) ion adsorption on to PLDC is a reversible process, it is possible for regeneration or activation of the adsorbent to reuse. The primary objective of regeneration is to restore the adsorption capacity of exhausted adsorbent while the secondary objective is to recover valuable components present in the adsorbed phase, if any. The adsorption of Mn(II) ion on PLDC id highly pH dependent; hence the desorption of Mn(II) ion ions are possible by controlling the pH. To find the most potential reagent for the desorption of Mn(II) ion , 5 ml of 0.01M acidic solutions (HCl,H_2SO_4,HNO_3) was mixed with 5 g/L Mn(II) ion adsorbed PLDC for enough time. The desorption efficiency of HCl, HNO_3, H_2SO_4 was found to be 97.60%, 89.80%,and 84.40% in the case of PLDC. Thus HCl is a most effective reagent was used for desorption process. The Mn(II) ion adsorption capacity of PLDC undergoing five cycles. It is observed that the Mn(II) ion adsorption capacity of PLDC is slightly decreases as increasing the cycle number.

Adsorption isotherms:

Adsorption isotherms are essential for the description of how metal ion concentration will interact with activated carbon (AC's) surface and are useful to optimize the use of AC's as adsorbents for the removal of manganese removal. The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the sorption mechanism. Several isotherm equations are available and three important isotherms are selected in this study, which are namely the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms. Both Freundlich and Langmuir models were used for the evaluation of experimental results.

The Freundlich model is as follows:

$$q_e=K_f C_e^{1/n} \tag{1}$$

Freundlich adsorption isotherm in its usual logarithmic form as follows:

$$Log (q_e) = 1/n \log (C_e) + \log (K_f) \tag{2}$$

Where, K_f and $1/n$ are the Freundlich constants, q_e is the amount of fluoride adsorbed per unit weight of the adsorbent (in mg/g), Ce is the equilibrium concentration of fluoride (in mg/L)[18].

Linear plots of log (C_e) Vs log (q_e) at different manganese ion concentrations are applied to confirm the applicability of Freundlich isotherm model for the removal of fluoride ions are shown in Figure 5 and the results were given in Table 6. The linear plot confirm about the monolayer coverage of manganese ions

on various adsorbent carbons at various concentrations of sorptive (temperature: 30 ± 1^{O}C) of Mn(II) ions at the surface of sorbent materials[19]. The Freundlich constants, i.e. K_f and $1/n$ for the systems were obtained by intercept and slope of the line. The numerical value of Kf and $1/n$ for PLDC are 0.19, and 0.38.. The fractional value of ($1/n$) indicates that the surface of sorbent is of the heterogeneous type with an exponential distribution of energy sites[20].The higher numerical values of K_f confirm the significant affinity of metal ions for AC's.

Langmuir isotherms:

The most important model of monolayer adsorption came from the work of Langmuir[21]. The Langmuir adsorption isotherm assumes that the adsorption can only occur at a fixed number of definite localized sites, each site can hold only one adsorbate molecule (monolayer), and the sites are homogeneous. Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as

$q_e = a \, b \, Ce \, / \, (1 + b \, Ce)$,

where *qe* is the amount adsorbed (mg/g) and *Ce* is the equilibrium concentration of adsorbate (mg/l), *a* and *b* are the Langmuir constants related to capacity and energy of adsorption, respectively. The linear form of the Langmuir isotherm can be expressed as,

1/qe = (1/ a) + (1/ b a Ce)

When $1/qe$ is plotted against $1/Ce$, a straight line with slope $1/ba$ is obtained which shows that the adsorption follows the Langmuir isotherm as shown in Figure 6. The Langmuir constants '*b*' and '*a*' are calculated from the slope and intercept with Y-axis.

The isotherm parameters along with the correlation coefficients (r-values) for adsorbents are presented in Table 6. The observed linear relationships as evidenced by r-values close to unity (0.9) confirm that these two adsorption isotherms are applicable.

The applicability of Langmuir isotherm model indicates the formation of monolayer coverage of adsorbate on outer surface of the adsorbent. Further, the essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor, and describe the type of isotherm defined by;

$R_L = 1/ (1 + b \, C_i)$

Where, C_i is the initial concentration of fluoride (in mg/L) and b is the Langmuir constant (in g/L). The separation factor R_L indicates the isotherm's shape and the nature of the adsorption process as unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$). In the present study the value of R_L (Table 6) for PLDC 0.37, , indicating that the sorption process is favorable for all these low-cost adsorbents. Where *b* and Ci are terms appearing in Langmuir isotherm. From Figure 5 and 6 it is found that the R^2 value for Langmuir model is near to unity (0.9 ± 0.1) and hence the process of defluoridation using treated bio-sorbents follows the Langmuir isotherm well. Table gives the calculations of Langmuir model for the removal of Mn(II) ion ions and the various constants of this model.

The Langmuir and Freundlich parameters for the bio-sorption of Mn(II) ion onto AC's are listed in Table 6. In other words, all of the isotherm models fit very well when the R^2 values are compared in Table 6.

CONCLUSION

The Pithacelobium dulce fruit shell seems to have very efficient and economical for removing toxic heavy metal ion such as Mn(II) from industrial waste water, for the preparation of the raw materials employed are widely available and inexpensive. Its metal ion binding capacity is appreciably high. Thus, it can be concluded that PLDC seems to be offer a very cheap and useful products for effective removal and recovery of toxic heavy metal ions from industrial ion can be recovered there by solving the problems of toxic effect of waste water on living organism, this also helps to solve waste water pollution problems.

Table-1: Effect of pH

pH	% Removal PLDC	Ce(mg/L)	Qe(mg/g)
5.00	82.35	1.765	1.6470
6.00	87.66	1.234	1.7532
7.00	92.26	0.774	1.8452
8.00	95.26	0.474	1.9052
9.00	97.80	0.324	1.9560

Table-2: Effect of adsorbate Concentration

Concentration	% Removal PLDC	Ce(mg/L)	Qe(mg/g)
5.00	95.30	0.235	0.9530
7.00	93.40	0.462	1.3076
10.00	90.00	1.000	1.8000
12.00	87.20	1.536	2.0928
15.00	82.80	2.580	2.4840
20.00	79.10	4.180	3.1640
25.00	76.00	6.000	3.8000

Table-3: Effect of adsorbent dose

Dose	% Removal PLDC	Ce(mg/L)	Qe(mg/g)
1.00	70.00	3.000	7.0000
2.00	82.00	1.800	4.1000
3.00	90.70	0.930	3.0233
4.00	95.30	0.470	2.3825
5.00	97.90	0.210	1.9580
6.00	98.70	0.130	1.6450
8.00	99.40	0.060	1.2425
10.00	99.60	0.040	0.9960
15.00	99.90	0.010	0.6660
20.00	100.00	0.000	0.5000

Table-4: Effect of Contact time

Time	% Removal PLDC	Ce(mg/L)	Qe(mg/g)
10	75.36	2.464	1.5072
20	80.40	1.960	1.6080
30	84.40	1.560	1.6880
40	88.00	1.200	1.7600
50	89.20	1.080	1.7840
60	89.50	1.050	1.7900
70	89.50	1.050	1.7900
80	89.50	1.050	1.7900
90	89.60	1.040	1.7920

Table-5: Effect of fluoride ion and Fe(II) ion concentration

Mn(II)ion concentration.	Fluoride ion Concentration Ci	PLDC Ce	% removal	Fe(II)ion concentration Ci	PLDC Ce	% removal
10	0.5	0.83	91.70	0.5	0.96	90.40
10	1.0	1.17	88.30	0.7	1.30	87.00
10	1.5	1.55	84.50	0.9	1.76	82.40
10	2.0	1.94	80.60	1.1	2.14	78.60
10	2.5	2.42	75.80	1.3	2.60	74.00
10	3.0	2.88	71.20	1.5	3.11	68.90
10	3.5	3.43	65.70	1.7	3.74	62.60
10	4.0	4.08	59.20	1.9	4.32	56.80

Table-6: Adsorption Isotherm parameters

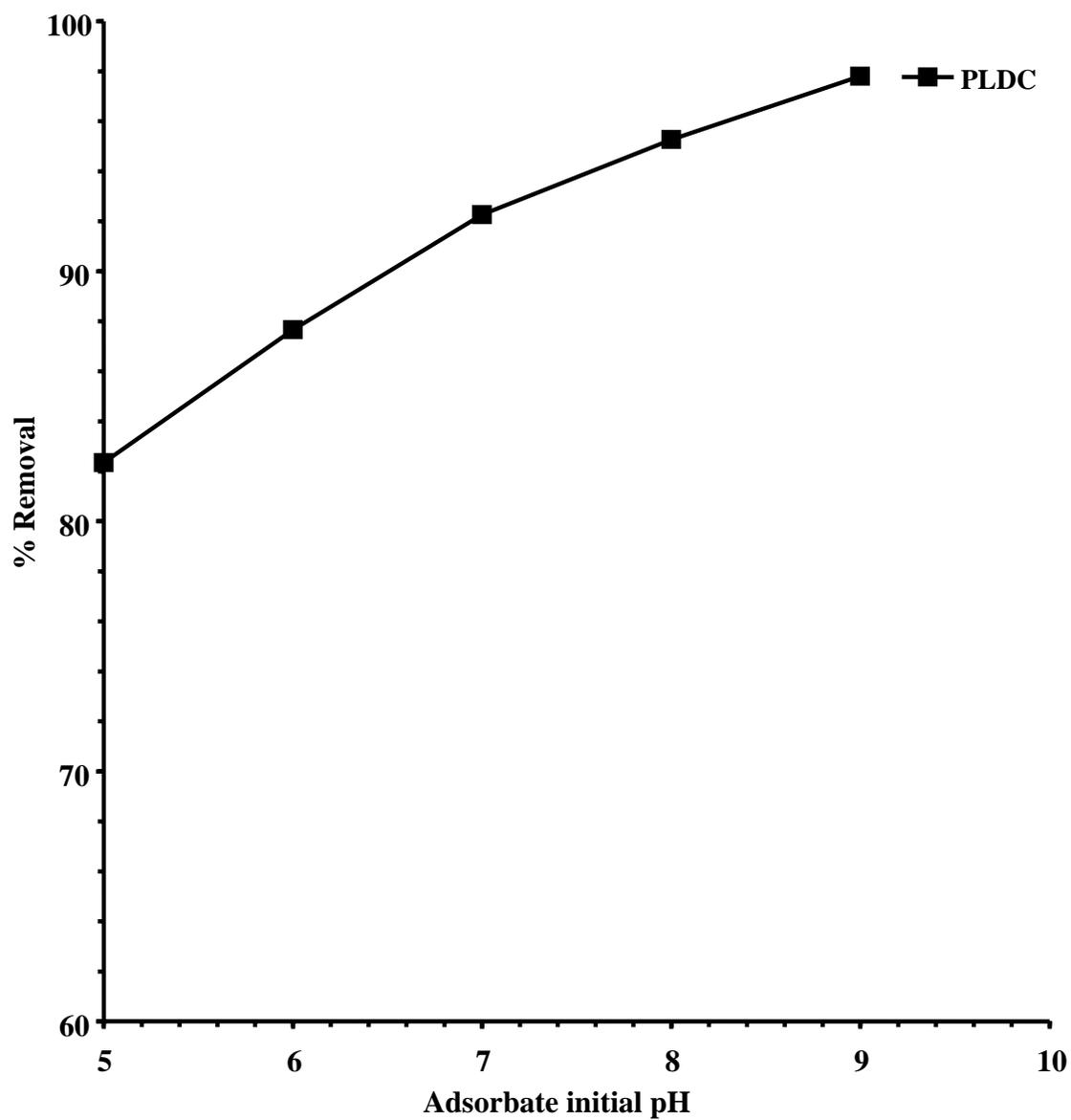| Isotherm	Parameter	PLDC
Langmuir isotherm	a	0.4156
	b	0.1638
	r	0.9792
	R^2	0.9587
	R_L	0.3791
Freundlich isotherm	K_f	0.1984
	1/n	0.3818
	r	0.9985
	R^2	0.9969

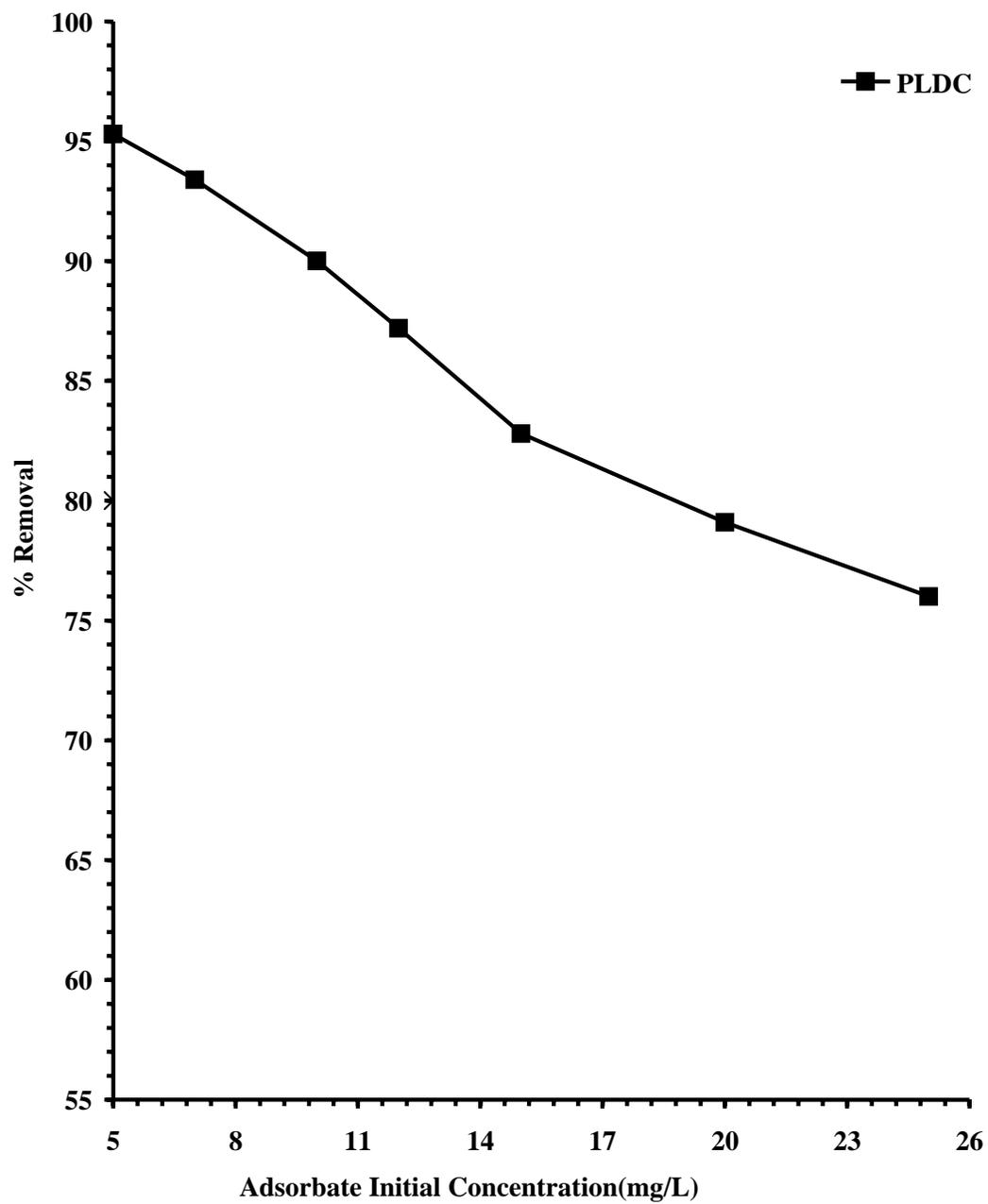**Fig.-1**:Effect of Adsorbate initial pH.

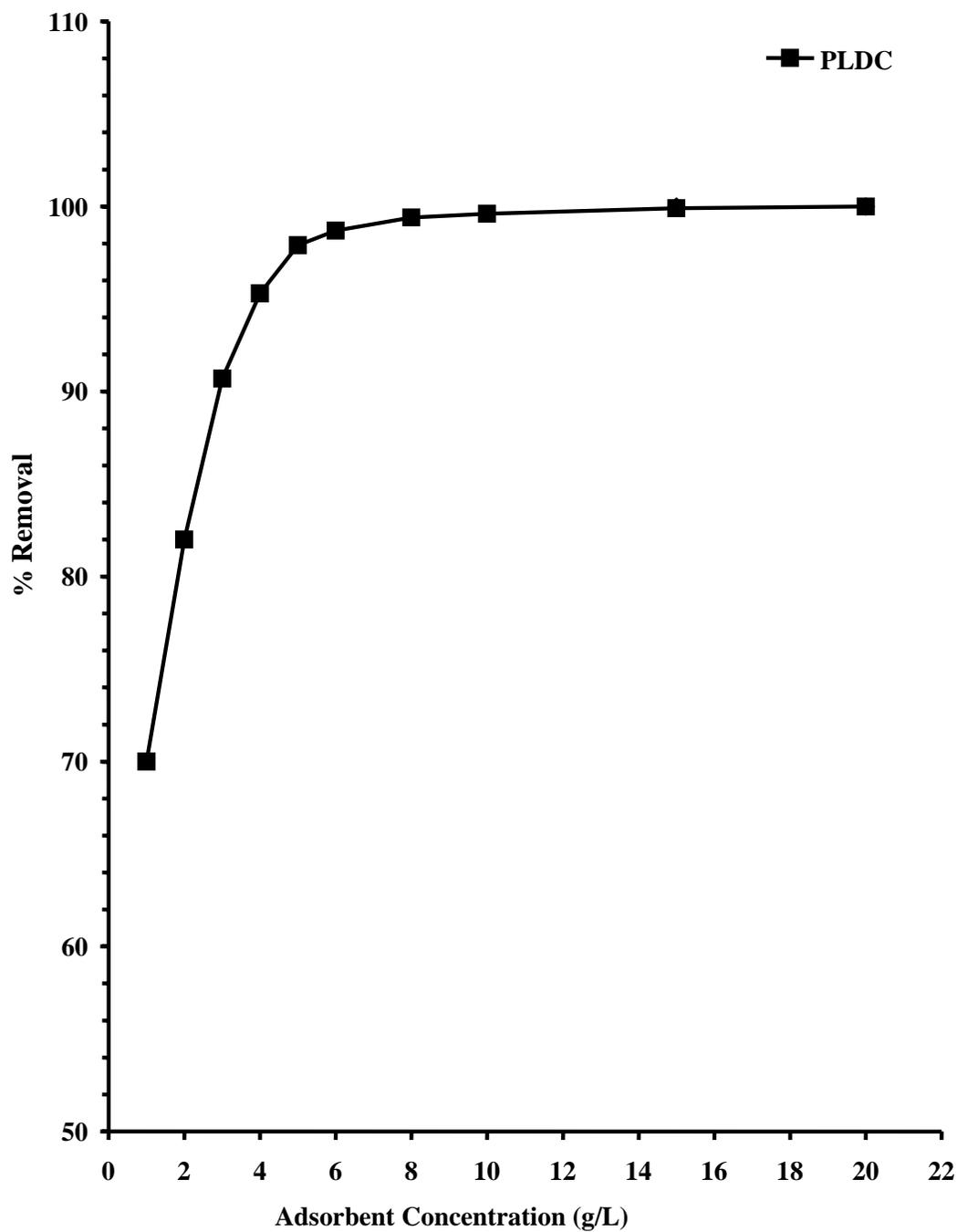**Fig.-2**:Effect of Adsorbate initial concentration.

Fig.-3:Effect of Adsorbent Dose.

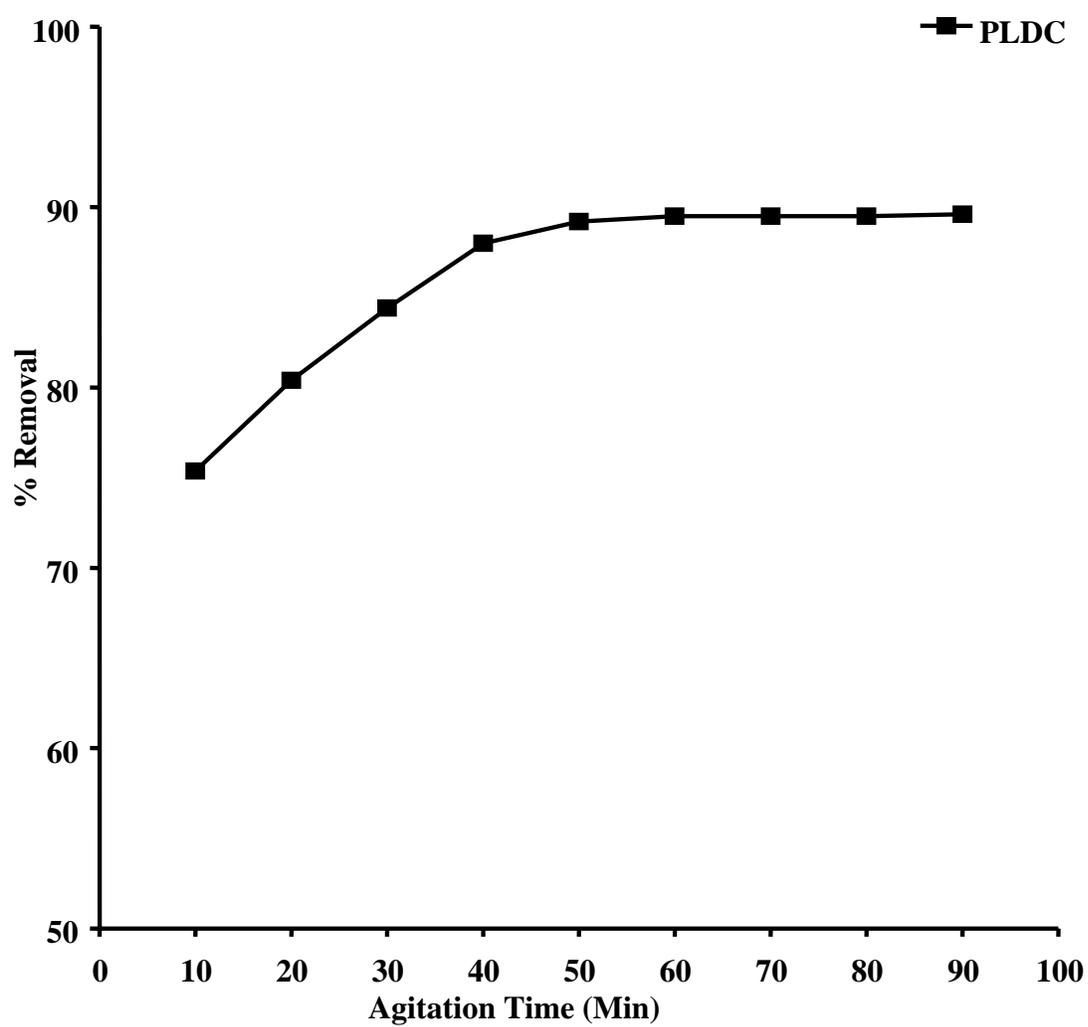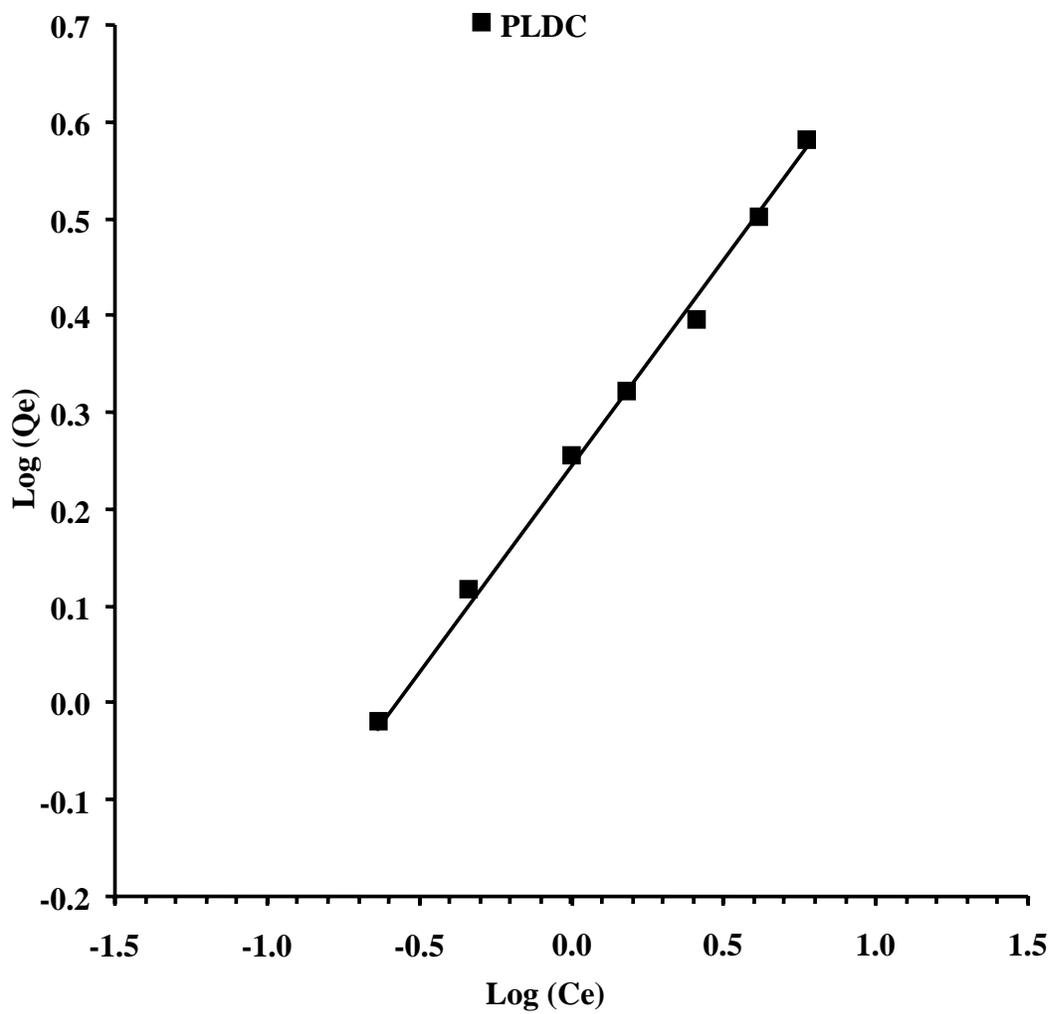**Fig.-4**:Effect of Contact time.

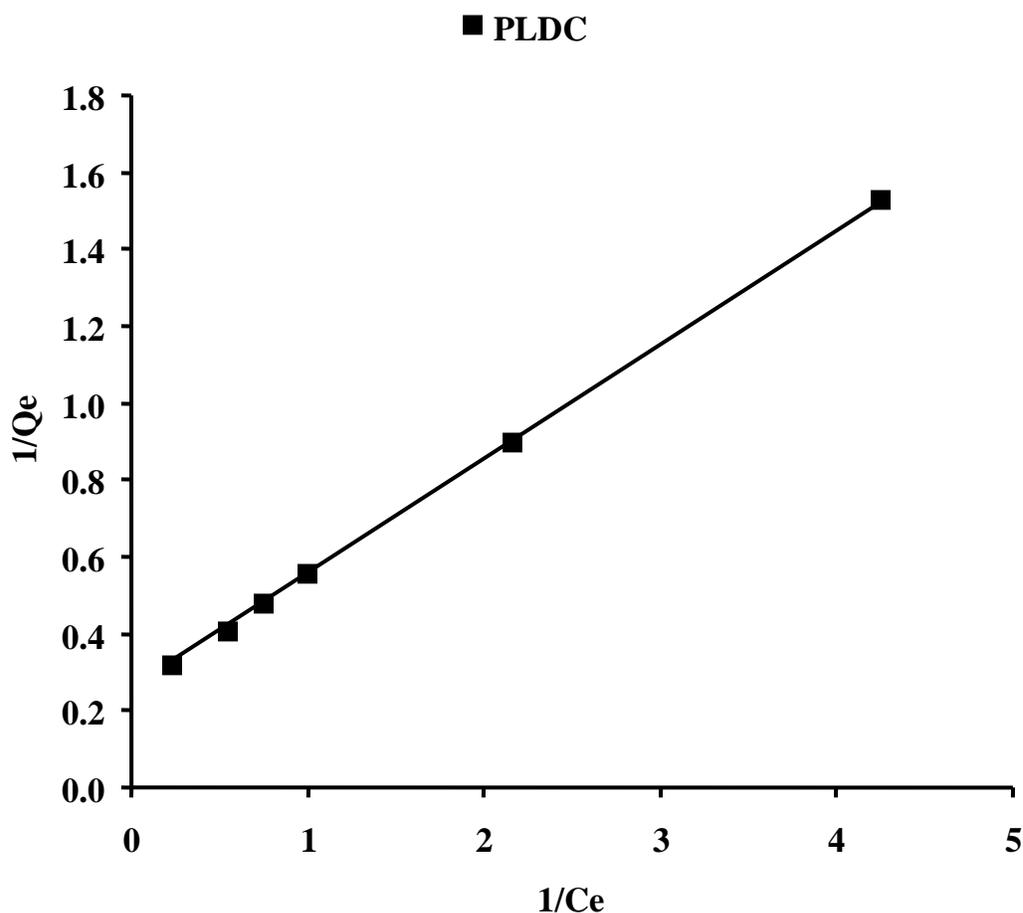**Fig.-5**: Freundlich isotherm.

■ PLDC

Fig.-6: Langmuir isotherm

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> We're in a giant car heading towards a brick wall and everyone's arguing over where they're going to sit.
> —David Suzuki