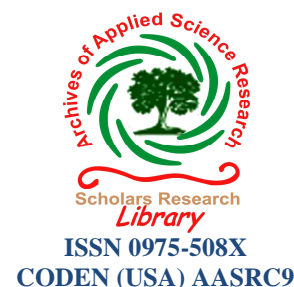




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Adsorption of Pb(II) Ions on Cucumis Melo peel activated carbon- A kinetic and equilibrium study

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ABSTRACT

In the present study, attempts have been made to use Cucumis Melo peel for the preparation of activated carbon with a view to use it in the treatment of wastewater and industrial effluent. The air-dried chopped Cucumis Melo peels are carbonized using sulphuric acid and characterized by the methods suggested by the Bureau of Indian Standards. It has been planned to study about the nature of the surface of the adsorbent using Scanning Electron Microscope and FTIR. Batch adsorption experiments were performed as a function of pH, contact time, solute concentration and adsorbent dose. The optimum pH required for maximum adsorption were found to be 6.0. The experimental equilibrium adsorption data are tested for the Langmuir, Freundlich, Temkin and Dubnin Isotherm equations and the results were interpreted. Adsorption kinetics data were modeled using the Lagergren, Elovich equations and intraparticle diffusion models. The results indicate that the First-order model best describes adsorption kinetic data.

Key words, Pb(II) ions, Teak Leaves, Activated Carbon, Lagergren, Elovich, Temkin, Dubnin, Langmuir, Freundlich, Low-Cost Adsorbent.

INTRODUCTION

The need for the use of water in virtually all human activities, whether urban, rural or industrial in nature, is undeniable. However, despite being of crucial important for human survival, this resource is associated with shortages that are partly due to the accumulated contamination of water resources over years of industrial exploitation. In recent years, the environmental organs concerned with the quality of the environment have established stricter environmental laws for the disposal of effluents, causing the chemical industry to increase investment in research with a focus on the treatment of its liquid effluents and solid wastes. Among the contaminants present in industrial waste, heavy metals receive considerable attention from scientists and engineers due to their toxic nature and the adverse effects of metals on the receiving water bodies. Unlike most organic pollutants, heavy metals are usually refractory and are not easily degraded [2]. As heavy metals are not decomposed into non-toxic end products, their concentrations should be reduced to acceptable levels before disposal into the environment[13].

The lead present in the wastewater of many industrial processes, such as the production of paint coatings, dyes, glass and batteries is potentially toxic to humans and to the aquatic environment. The main consequences in the

environment are the poisoning of aquatic organisms and severe changes in the aquatic fauna and flora. For humans, constant exposure to lead causes edema, learning disabilities in children, damage to organs such as the liver, kidneys and heart, and immune system disorders [8]. The maximum lead discharge into receiving bodies allowed by Brazilian legislation is 0.5 mg L^{-1} and the current limit according to the USEPA for drinking water is 0.015 mg L^{-1} [6].

There are various techniques available for the removal of heavy metals from aqueous effluents aimed at minimizing their impact. Chemical precipitation is the most commonly used method in large scale and requires subsequent stages of sedimentation and filtration before the treated water can be reused. However, for the decontamination of large volumes of effluents containing metal ions at low concentrations the process is unsuitable because of the low efficiency and high operating costs associated with this extraction process. Other methods widely used for removing heavy metals from wastewater include ion exchange, reverse osmosis, evaporation and membrane filtration. Many of these methods have drawbacks such as high costs associated with the installation, operation and sludge disposal, and some of them are not appropriate for small scale industries. Furthermore, the identification of cost-effective methods for the removal of heavy metals at low concentrations represents a difficult challenge. In this regard, the adsorption process is highly effective and economical. For this reason, the study of adsorption has grown significantly in recent years, leading to research on the development and optimization of increasingly selective adsorbents.

In recent years, the search for low-cost adsorbents that have metal binding capacities has intensified. Agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, banana pith, soybean and cotton seed hulls, peanut shells, hazelnut shell, rice husk, saw dust, wool, orange peel, compost and leaves [4]. The present investigation describes the preparation of activated carbon (CMAC) from Cucumis Melo peel and its characterization. The study is aimed at to remove Pb(II) ions from wastewaters by adsorption technique using CMAC as the adsorbent. Batch mode experiments were conducted to determine the effect of pH, contact time, solute concentration and adsorbent dose. Kinetics of the experiments was arrived at by employing Lagergren, Elovich equations and intraparticle diffusion models. Langmuir, Freundlich, Temkin and Dubnin adsorption isotherms were also employed to determine the adsorption capacity of the adsorbent for the removal of Pb(II) ions.

MATERIALS AND METHODS

Adsorbent

Preparation, Cucumis Melo peel was collected from in and around pazhamudir nilayam of Coimbatore. The collected peels were cut into small pieces, washed with tap water several times to remove dust and dirt and rinsed with deionised distilled water and then dried. Cucumis Melo peels were placed in the muffle furnace and carbonization was carried out at 200°C for 2 hrs. The activated carbon thus obtained (Here after **CMAC**) was ground well, sieved and the adsorbent of the size $75\text{-}125\mu\text{m}$ has been used for the present study.

Characterization, IR spectrum of CMAC was recorded (Thermo Nicolet, Nexus 670) in the range of $4000 - 450 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . SEM images of the surface of the CMAC were obtained using LEO 1445 VP Scanning microscope. The physico-chemical characterization of CMAC, such as moisture content, ash content, matter soluble in water, matter soluble in acid, pH, apparent density have been determined by the methods suggested by the Bureau of Indian Standards [ISI] [5]. The surface area and pore specific volume were determined by BET method.

EXPERIMENTAL PROCEDURE

The adsorption experiment were performed in a batch mode in a series of beakers equipped with mechanical shaker by agitating 250mg of the chosen adsorbent with 50ml of metal ion solution with known previously determined, initial concentration of the considered heavy metal ion and the required initial pH value. The suspension was filtered and the remaining concentration of metal in the aqueous phase was determined. The final pH value was also measured. Batch adsorption experiment were performed by contacting 250mg of the selected activated samples with 100ml of the aqueous solution of different initial concentrations ($100, 200, 300, 400 \text{ mg/l}$) of natural solution pH. The experiment were performed in a mechanical shaker at controlled temperature ($25 \pm 2^\circ\text{C}$) for a known period of time ranging between 10 to 210min. At the end of the predetermined time, the suspension was filtered, the remaining concentration of Pb(II) in each sample after adsorption at different time intervals was determined by spectrophotometer after filtering the adsorbent with Whiteman filter paper to make it carbon free. The batch process

was used so that there is no need for volume correction. The Pb(II) concentration retained in the adsorbent phase was calculated according to

$$q_e = (C_i - C_e)V/W$$

where C_i and C_e are the initial and equilibrium concentration (mg/l) of Pb(II) solution respectively. V is the volume and W is the weight (g) of the adsorbent.

RESULTS AND DISCUSSION

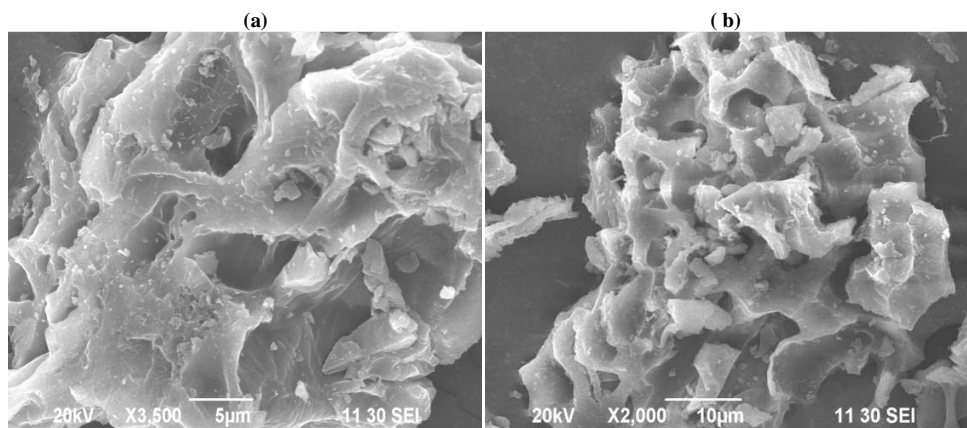
Table.1 shows the comparative values [9] of characteristics of commercial activated carbon (CAC) with CMAC. It is found from Table.1 that the bulk density values for CMAC (0.2418 g /cc) is comparable with that of CAC. The other physicochemical characteristics like ash content, matter soluble in water and acid are also comparable with those of CAC. The pH value suggested that the carbon chosen may be considered to have the characteristics of CAC.

Table.1-Characteristics of CAC and CMAC

S.No.	Characteristics	CAC	CMAC
1	Bulk Density, g/cc	0.68	0.2418
2	Moisture Content, %	12.57	10.18
3	Ash Content, %	2.91	2.83
4	Matter Soluble in Water, %	1.55	1.80
5	Matter Soluble in Acid, %	4.58	4.77
6	pH	9.2	6.55
7	Surface Area, m ² /g	296	362

A scanning electron microscope (SEM) was used to examine the surface of the adsorbent and the SEM photographs. **Figure. 1** shows the surface morphology of the natural CMAC and metal loaded CMAC. CMAC is a heterogeneous material consisting largely of small spheres, irregular and porous cell wall of plant cells. The surface seems to be rough and protrusions. Pores can be seen however, not extending into the matrix.

Figure 1. SEM images of CMAC (a) natural CMAC at 5 μ m(a),10 μ m(b), Pb(II) loaded 10 μ m(c) 5 μ m(d)



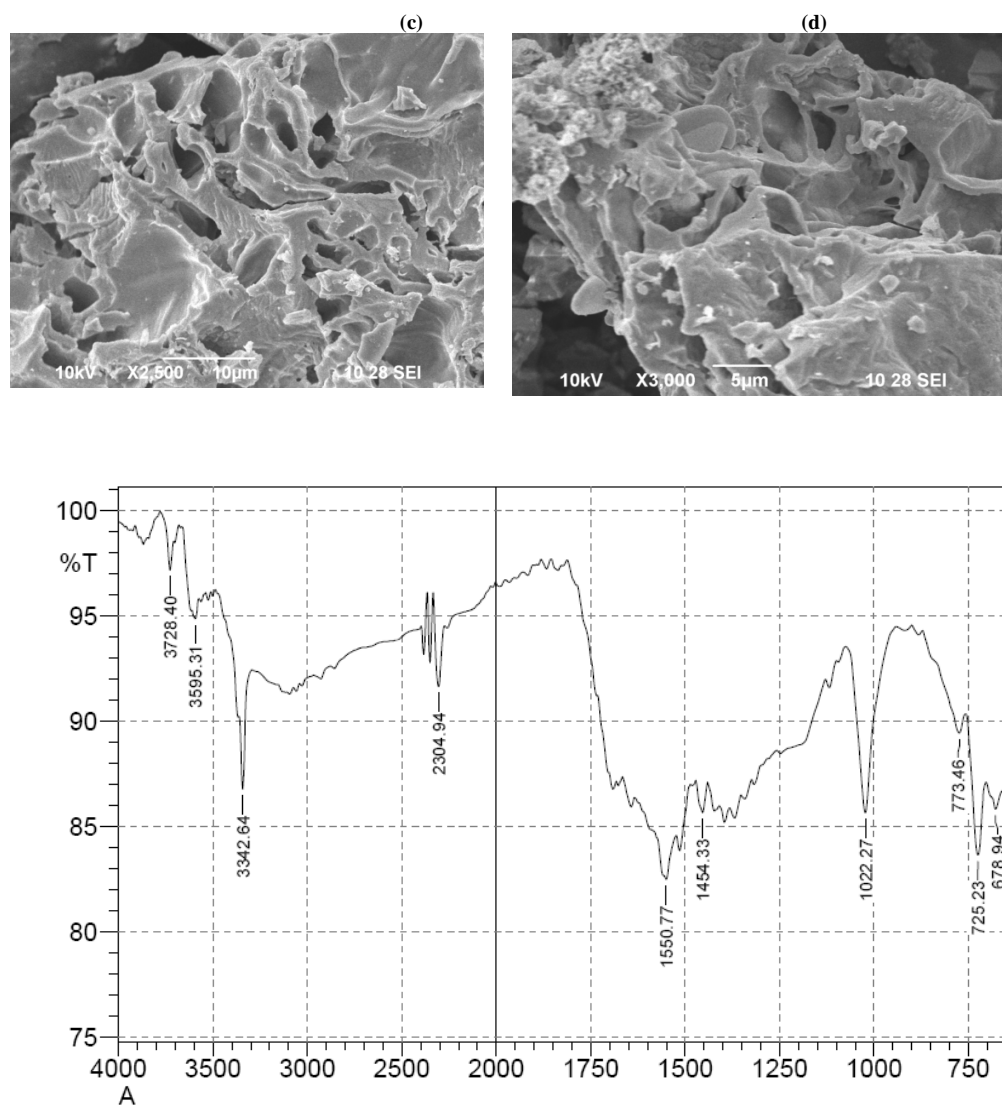


Figure 2. Analysis of the IR spectrum has been used to explore the complete surface characteristics of the adsorbent

FTIR spectroscopy is one of the most versatile and powerful analysis methods for IR data and has been used as a qualitative technique for the evaluation of the chemical structure of the carbon materials [7]. **Figure. 2** presents the fundamental peaks of the adsorbent.

A broad and strong band stretch in the region between 3700cm^{-1} and 3595cm^{-1} indicates the presence of hydrogen bonded $-\text{OH}$ groups. The sharp peak at 3342cm^{-1} is due to N-H stretching. The position of absorption depends upon the degree of hydrogen bonding. The band at 2304cm^{-1} corresponds to the presence of $-\text{C}=\text{C}$ stretching vibrations arising from groups such as alkynes, cyanides and isocyanates. The band obtained at 1550.77cm^{-1} was due to the asymmetric stretching of NO_2 group. The band observed at 1022.27cm^{-1} was due to C-O stretching of $\text{C}=\text{C-O-C}$ group. The band observed at $770\text{-}730\text{cm}^{-1}$ shows monosubstitution on the aromatic ring. The IR spectrum of the adsorbent CMAC supported the presence of $-\text{OH}$, $-\text{C}=\text{C}$, $-\text{NH}_2$ and $-\text{NO}_2$ C-O-C functional groups present on the surface of CMAC. The functional groups present on the Cucumis Melo peel surface seem to play an important role in metal adsorption. The adsorption Pb(II) onto CMAC may be due to formation of hydrogen bonds formed between the metal ions and the adsorbent. Hydrogen bonds would occur between hydroxyl, amine and Nitro groups present on the adsorbent with the metal ions [18].

It has been reported [15] that pH of wastewater is a significant controlling factor in the adsorption process. Literature survey has revealed that the Pb(II) ions were adsorbed only at less acidic medium (i.e.) at the pH range of 5-6. Hence, experiments were conducted using a lead nitrate solution of concentration around 100 mg/l with the pH of 6.0 at different doses viz., 100, 150, 200, 250, mg/l. The percent removal of Pb(II) and the corresponding doses are given in Table 2. During the process of adsorption, the rate of removal of Pb²⁺ ions increases with increasing time, up to a certain period and thereafter the rate of removal of solute becomes constant. At one stage, it may even become insignificant and such a trend is observed in the plot of % of solute removed against contact time (Figure. 3) in which the curve becomes asymptotic to the axis of contact time after a certain period. Such a curve represents nearly an equilibrium pattern.

Table 2. FTIR peak assignments of functional groups on carbon surfaces

Group or Functionality	Wave number assignments (cm ⁻¹)
Alcohol group Free O-H group (Stretching)	3700-3500
Primary amides N-H (Stretching)	3342
-C=C (Stretching)	2304
-NO ₂ (asym Stretching)	1550.77
Ether group -C-O (Stretching)	1022.27
Aromatic Ring C-H bonding for mono substituted benzene	770-730

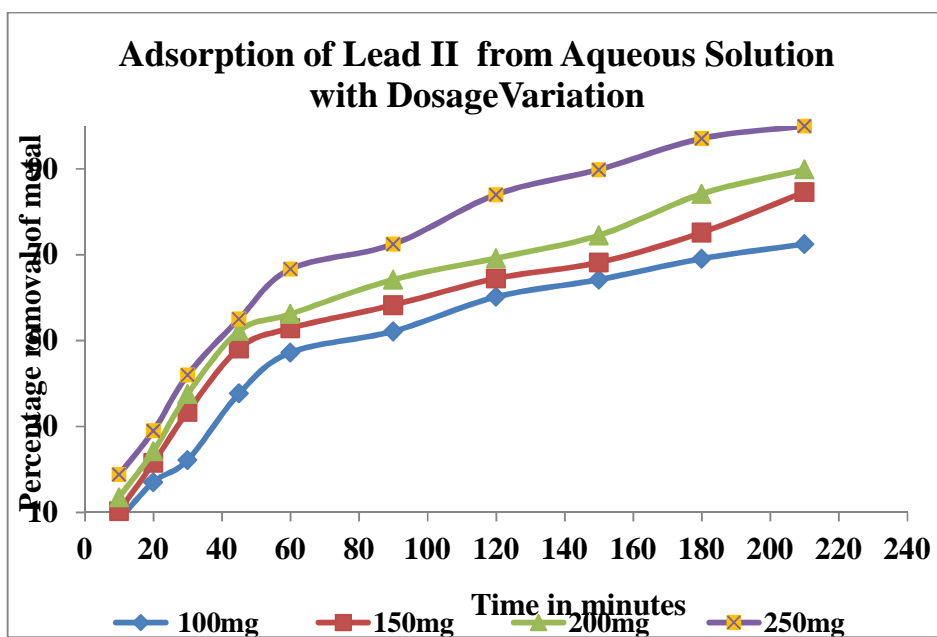


Figure 3. Adsorption of Lead II from aqueous solution with dosage variation

It is understood from the figure that the residual concentration of Pb(II) ions in the adsorbate solution drops steeply in the first 210 min and then gradually decreases to a constant value. The initial steep drop of the residual concentration of Pb(II) ions is due to the rapid removal of Pb(II) ions which occurs as a result of the presence of large number of active adsorption sites available on the surface of the adsorbent, compared to the number of adsorbate species in the solution. Hence for all practical purposes, 210 min is presumed to represent equilibrium time which means that 210 min appears to be sufficient for the maximum adsorption of Pb(II) ions by the chosen adsorbent, under a given set of experimental conditions. The maximum amount of Pb(II) ions adsorbed corresponding to the equilibrium is found to be 72.5 % for a weight of 100mg/l of the adsorbent. The curves in the figure (Figure. 3) are single, smooth and continuous suggesting the probability of formation of monolayer coverage

of Pb(II) species on to the outer surface of the adsorbent. The nature of the curve indicates the uptake of Pb(II) ions per unit mass of adsorbent increases with the increasing dose of the adsorbent.

Table.3-Effect of contact time on lead removal

Time in minutes	Removal of Lead(II) in Percentage			
	100mg	150mg	200mg	250mg
10	8.24	10.32	13.5	18.84
20	17.08	21.55	24.23	28.99
30	22.2	33.45	37.56	42.03
45	37.7	48.2	52.25	55.07
60	47.23	52.92	56.2	66.67
90	52.2	58.3	64.23	72.46
120	60.2	64.5	69.21	84.06
150	64.2	68.23	74.55	89.86
180	69.1	75.2	84.2	97.1
210	72.5	84.6	89.9	—

Table.3 presents the values of the amount of Pb(II) adsorbed at 30min as 22.2, 33.45, 37.56, 4.03%, when the concentration of the adsorbent is 100, 150, 200, and 250 mg/l respectively, and at 210min the corresponding Pb(II) removal is 72.5, 84.6, 89.9, and 97.1 %. This shows that as the dose of the adsorbent increases, the adsorption of lead also increases. The minimum time required to achieve maximum adsorption decreases with the increase in the dose of the adsorbent which may be attributed to the increase of the surface area. In other words, the number of available active sites may be more compared to the number of adsorbate species. The experimental data obtained for the adsorption of Pb(II) on to the surface of CMAC under the given set of conditions, were analyzed in the light of Lagergren model with the view to evaluating the mechanistic parameters associated with the process of adsorption.

Lagergren equation [16] is

$$\log_{10} (q_e - q) = -k_{\text{Lager}} t / 2.303 + \log_{10} q_e$$

where, q_e is the amount of metal ions adsorbed at equilibrium, q is the amount of metal ions adsorbed at time(t), k_{Lager} is the overall rate constant for the adsorption process.

Figure. 4 –Kinetic Modelling for Adsorption of Lead (II) from aqueous solution using Lagergren Equation

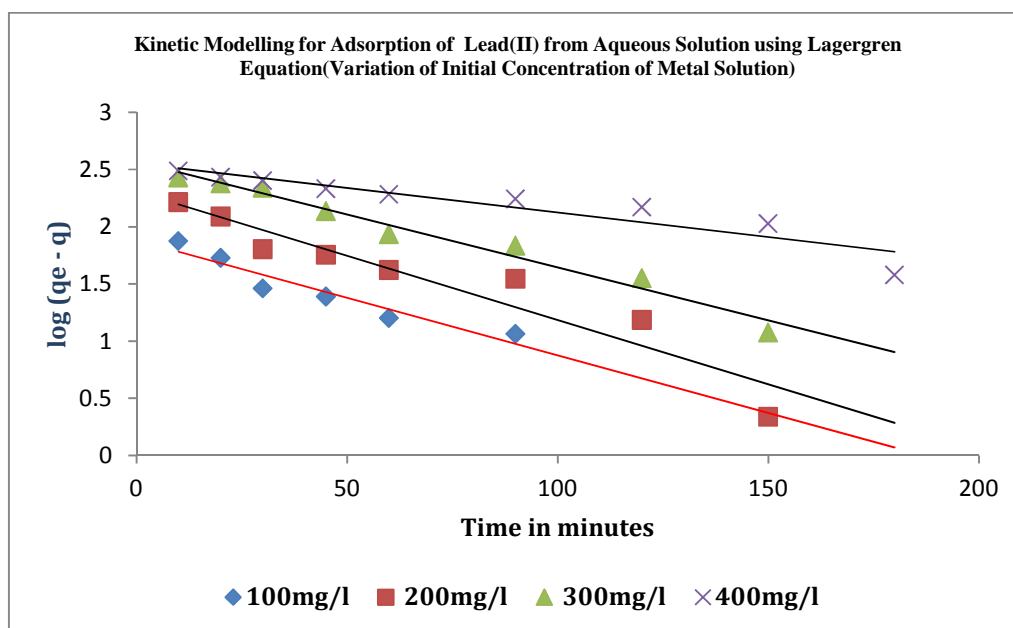


Table.4-Effect of dose on k_{Lager} and $k_{Elovich}$

S.No	Adsorbent Dose (mg/l)	K_a in $\text{min}^{-1} \times 10^{-2}$	Initial adsorption rate constant (α) $\times 10^2$
1	100	1.3081	6.074
2	150	1.8885	3.2477
3	200	2.146	3.4834
4	250	2.2962	2.5646

The Lagergren equation suggests linearity for the plot of $\log_{10} (q_e - q)$ against time, t . The Figure.4 represents the relation between $\log_{10} (q_e - q)$ and t under a given set of experimental conditions from the slope of each line, the rate constants were determined. The values of k_{Lager} obtained for different doses of the adsorbents are presented in Table. 4.

The rate constant K_a decreases with increasing initial concentration of the dye solutions used in this study. The reason for this behaviour can be attributed to the high competition for the adsorption surface sites at high concentration which leads to lower adsorption rates[14].

The results obtained in the light of Lagergren were further confirmed by Elovich equation is given as follows,

The Elovich equation was developed to describe the kinetics of chemisorption of gases onto solids and it is generally expressed as,

$$dq_t/dt = \alpha \exp(-\beta q_t)$$

where,

' q_t ' is the amount of dye adsorbed (mg/g) by the adsorbent at time 't'

' α ' is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and

' β ' is the desorption constant (g mg^{-1}) during any experiment.

Assuming the initial boundary condition, $q = 0$ at $t=0$, the above equation on integration become,

$$1/q_t = 1/\beta \ln(1 + \alpha\beta t)$$

To simplify the Elovich's equation, Chien and Clayton (1980) assumed $\alpha\beta \gg 1$ and applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, equation becomes [12]

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$$

This equation is commonly used for the chemisorption, which is probably the mechanism that controls the rate of adsorption. This model can be applied with success in liquid solution [3]. Elovich plots of $\ln t$ vs q (amount of Pb(II) adsorbed (mg/g) by the adsorbent at time 't') gives a linear relationship with a slope of $1/\beta$ and an intercept of $1/\beta \ln(\alpha\beta)$. The Elovich equation data obtained in this study for the adsorption of Pb(II) from aqueous solution onto CMAC are given in Table.4.

The higher value of initial adsorption rate (α) may be due to the greater surface area of the adsorbent CMAC, for the immediate adsorption of Pb(II) from aqueous solution and also from industrial effluent. The decrease in the value of desorption constant (β) with the increase of the initial concentration of the metal solutions [12].

Langmuir adsorption isotherm was developed by Irvin Langmuir describe the surface coverage of adsorbate on a solid surface. Langmuir adsorption isotherm is based on the assumption that points of valency exist on the surface of the adsorbent and that each of these sites is capable of adsorbing only one molecule. Thus, the adsorbed layer will be one molecule thickness. Further, it is assumed that all the adsorption sites have equal affinities for the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site[10]. The intermolecular forces decrease rapidly with distance, and consequently the existence of monolayer coverage of the adsorbate at the outer surface can be predicted [11]. The Langmuir adsorption isotherm is generally expressed as

$$m/x = 1/(k_1/k_1') + 1/k_1 C_e$$

The linear plot of $1/C_e$ versus m/x obtained in this study shows the applicability of Langmuir adsorption isotherm indicating the formation of monolayer coverage of adsorbate on the surface of the adsorbent Blue-Green Algae.

Separation Factor (R_L), The effect of isotherm has been taken into consideration with a view to predict whether the studied adsorption system is favourable or unfavourable. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter ' R_L ' which is defined as

$$R_L = 1 / 1 + bC_0$$

where,

C_0 is the initial concentration of the dye solution and

b is the Langmuir constant.

In this study, R_L values obtained are found to be less than one and decreased with increasing initial concentration of the dye solution, confirming the favourable uptake of the dyes onto CMAC adsorbent [17]. The Langmuir model shows the best fit with the highest correlation coefficient (r^2) values in the range of 0.986-0.995, indicates the feasibility of the adsorption of the metals from aqueous solution and from industrial effluents using the adsorbent CMAC, also suggest the monolayer coverage of the metals onto CMAC [19] and the homogeneous distribution of active sites on the surface of the adsorbent CMAC.

Freundlich isotherm,

$$\log q_e = \log K_f + 1/n \log C_e$$

where, q_e is the amount of metal ions adsorbed (mg/L) ; C_e is the equilibrium concentration of the adsorbate species (mg/l) ; K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. When $\log q_e$ is plotted against $\log C_e$, a straight line with slope $1/n$ and intercept $\log K_f$ is obtained. This reflects the satisfaction of Freundlich isotherm model for the adsorption of Pb(II) ions.

The Freundlich parameters for the adsorption of Pb(II) ions are given in Table 5. The intercept of the line, $\log K_f$ is roughly an indicator of the adsorption capacity and the slope $1/n$ is an indication of adsorption intensity [1].

Table.5 Langmuir and Freundlich constants for the adsorption of Pb (II) at 25 °C

Adsorbent	Langmuir constants			Freundlich constants		
	$1/k_1$	R_L	R^2	K_f	$1/n$	R^2
CMAC	0.0633	0.9937	0.987	10.59	0.5039	0.989

CONCLUSION

It is found from the characterization study that the selected adsorbent, CMAC, is expected to have more adsorptive capacity, and hence it acts as a suitable adsorbent for the removal of Pb(II) ions from aqueous solution of lead nitrate. The adsorption data suggest that the pH of the solution is the most important parameter in the control of metal ion adsorption on to the CMAC. This study has shown the ability of the adsorbent to adsorb metal ions only in less acidic medium. Hence the batch mode studies were carried out at pH 6.0. The equilibrium time 210 min appears to be sufficient for the maximum adsorption of Pb(II) species by CMAC, and under the given set of experimental conditions, the maximum amount of Pb(II) adsorbed is found to be 72.5 %. The percent removal of Pb(II) from wastewaters increases with the increasing dose of the adsorbent that the minimum time required to achieve maximum adsorption decreases with the increase of the dose of the adsorbent. The conclusions derived from the study of applicability of Lagergren, Elovich, Langmuir and Freundlich isotherm to the present system revealed the first order kinetic nature of the adsorptive process.

Detailed literature survey has revealed the applicability of only little work on record concerning the use of CMAC as the adsorbent for the removal of lead. All the above information revealed that the chosen adsorbent namely CMAC ,

may be used as a suitable adsorbent for the removal of not only Pb(II) ions but also any heavy metal ions from wastewaters.

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