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Adsorptive Removal of Pb(II) from Aqueous Solution Using Chemically Activated Mixed Adsorbents

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Heavy metal ions released from industries cause toxicity and posses threat to the living organisms. In this study, removal of Pb(II) from aqueous solution is done by adsorption using coconut shell chemically activated carbon (CSCAC) and cashew nut husk chemically activated carbon (CNHCAC) with different proportions have been investigated. The influence of various parameters including effect of pH, carbon dose and equilibration time were determined. The quantitative removal of Pb(II) occurs, when batch studies were done at an optimum carbon dose of 0.08 g, pH of 3 and equilibration time of 2 h for the mixed adsorbent in 1:1 proportion. 0.2 M HCl was found to be suitable to desorb the Pb(II) quantitatively. Adsorption isotherms on adsorbents were determined and correlated with isotherm equations such as Freundlich, Langmuir and Temkin models and found to be more suitable for Langmuir adsorption isotherm. Kinetic studies showed that a pseudo second order model was more suitable. The mixed adsorbent (CS-CNHCAC) was found to be of low-cost, abundant and promising for the removal of Pb(II).

Keywords: Coconut shell, Cashew nut husk, $Na_2S_2O_8$, Chemical activation, Mixed adsorbent, Desorption.

INTRODUCTION

Lead(II) is one of the oldest known toxic heavy metal ions. The presence of Pb(II) in industry was found many years ago and it played an important role in morbidity and mortality at the time of industrial revolution. Even a trace amount of Pb(II) in the environment can cause severe health hazards to mankind and many control measures were taken to limit the exposure of lead.

The main sources of Pb(II) effluents are electroplating and paint industries. The airborne Pb(II) from paint settles in the dust and soil, which results in significant hazardous effects and children are more sensitive to bear the burden of Pb(II) exposure[1]. Lead poisoning occurs occasionally leading to lower blood levels and birth weight loss of infants[2]. Another source of Pb(II) is the soldering mechanism which is used in the electronic industries.

The presence of heavy metal ion in the aquatic environment added a deal to scientists because of their toxic nature. Even a small concentration of Pb(II) in water can cause damage to kidney, nervous system and sickness in brain leading to death. It is found that the industrial water has 200-500 mg/L Pb(II) and according to water quality standards, it should be in the range of 0.05 mg/L.

In the recent years, the public concern over water quality, discharging the industrial wastewater containing Pb(II) is stringently regulated to reduce environmental hazards. Hence, extraction of heavy metal ions from various industrial effluents becomes an imperative issue from an environmental point of view[3].

The commonly used techniques for removing heavy metal ions are precipitation, ion-exchange and electrochemical methods. Aquatic plants, agricultural by-products and some micro-organisms also have the ability to accumulate heavy metal ions[4]. However, the high cost, incomplete reactions, disposal of sludge, low selectivity, high energy requirements and formation of toxic slurries make the above mentioned techniques an impractical one[5]. The natural clay, modified with some polymeric material can also be used as an adsorbent. They have high stiffness and strength so that it is very difficult to remove them separately from the main components.

Adsorption is one of the concepts used in the removal of Pb(II) from aqueous water waste because of its high efficiency, low cost and simple operation steps[6,7]. Both the bio-sorption and chemical adsorption plays a significant role than the traditional way of removing metal ions. The adsorbent used are the materials containing vegetation matters such as paddy

husk, tamarind nut, coconut shell, wood bark *etc*., and the adsorptive properties of the activated carbon are well studied[8]. The cost of good quality of commercial activated carbon is reasonably high and therefore it is decided to search for low-cost adsorbents. Not much studies were focused on the potentiality of mixed adsorbents, hence this work investigates the low cost adsorbents such as coconut shell and cashew nut husk in chemically activated form and they were mixed and can be used for the removal of Pb(II) from aqueous solutions.

EXPERIMENTAL

Preparation of adsorbents: The chemically activated carbon was prepared by mixing coconut shell pieces with concentrated sulphuric acid in 1:1.5 weight ratio in the presence of 0.1 part of sodium per-sulphate ($Na_2S_2O_8$) and the resulting char was kept in an air oven at 110 °C for 10-12 h. The chemically activated material was thoroughly washed with water followed by 2 % solution of sodium bicarbonate until effervescence had ceased and then it was left soaked in 2 % solution of sodium bicarbonate overnight. The chemically activated material was then separated, washed with distilled water to remove the free acid and dried at 105 ± 5 °C. The carbon obtained from coconut shell was grounded well and sieved to particle size ranging from 20-50 ASTM mesh size. The carbon thus prepared was designated as coconut shell chemically activated carbon[9].

Similarly, cashew nut husk chemically activated carbon is also prepared for adsorption studies. Both the prepared carbons were then mixed together in 1:1 proportion (CS-CNHCAC) and the three types of chemically activated carbons were tested for the effective removal of Pb(II).

Evaluation of carbon characteristics: The materials such as CSCAC, CNHCAC and CS-CNHCAC were used as adsorbent materials. It was characterised for relevant parameters before conducting the experiments. The important carbon characteristics of CSCAC, CNHCAC and CS-CNHCAC such as bulk density, moisture content, ash content, matter soluble in water, matter soluble in acid, pH, de-colorization property, ion exchange capacity, surface area and iron content were carried out and the results are tabulated in Table-1.

TABLE-1
CARBON CHARACTERISTICS

S. No	Control tests	CSCAC	CNHCAC	CS-CNHCAC
1	Bulk density (g/cc)	0.65	0.56	0.69
2	Moisture (%)	5.00	7.00	5.50
3	Ash (%)	0.39	0.44	0.42
4	Matter soluble in water (%)	0.95	1.33	0.87
5	Matter soluble in 0.25M HCl (%)	2.23	2.49	1.55
6	Decolorizing power (mg/g)	12	18	15
7	Ion exchange capacity (meq/g)	1.0	0.5	0.6
8	Surface area, m^2/g [N^2-BET]	80	72	102
9	pH	6.50	6.14	6.46
10	Iron content (ppm)	0.2445	0.3384	0.2915

It is evident from Table-1 that the bulk density of the CS-CNHCAC is superior over other carbons which suggests that it could been used for the removal of Pb(II) from wastewater. Also it is clearly evident that from the characteristics among these three carbons, the mixed adsorbent (CS-CNHCAC) is dominant over other carbons.

Batch studies: Batch studies were carried out using orbital mechanical shaker agitated at a constant speed of 150 rpm. 100 mL of 20 mg/L of Pb(II) were adjusted to different initial pH values using H_2SO_4 or NaOH and were taken in 300 mL polythene bottles for known amounts of CSCAC, CNHCAC and CS-CNHCAC. The solutions were equilibrated for 24 h for different pH values in the range of 1-10. After the equilibration period, the solutions were filtered and analysed for Pb(II) by using atomic absorption spectrophotometer at 217.0 nm. Other parameters such as effect of carbon dose at optimum pH and effect of equilibration time under optimum pH were also established by the above method.

Desorption studies: The reversibility of adsorption was investigated by carrying out desorption experiments. Desorption of metal ions was studied by using different concentrations of hydrochloric acid (0.05-1 M) with adsorbents CSCAC, CNHCAC and CS-CNHCAC.

Adsorption isotherms: Adsorption isotherms are mathematical models that describe the distribution of the adsorbate among liquid and solid phases, based on the heterogeneity/homogeneity of the solid surface, the type of coverage and the possibility of interaction between the adsorbate. Adsorption isotherm studies were carried out with different initial concentrations of Pb(II) and fixed doses of carbon and pH values. In this study, equilibrium data were analyzed using the Freundlich, Langmuir and Temkin isotherm expressions[10].

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface[11]. The equation is commonly represented in linear form as,

$$\ln\frac{x}{m} = \ln K_f + \frac{1}{n}\ln C_e \quad (1)$$

where, x is the amount of solute adsorbed in mg/L, m is the weight of the adsorbent in g/L, K_f is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent in mg/g, n is the Freundlich equation exponent that represents the intensity of adsorption in L/mg, C_e is the equilibrium concentration of the solute in mg/L.

The Langmuir model assumes that uptake of the metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions[12]. In linear form, the Langmuir equation may be written as,

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

where, C_e is the equilibrium concentration in mg/L, q_e is the amount adsorbed at equilibrium concentration of the metal ion in mg/g, Q_0 is the Langmuir constant related to the maximum amount of adsorbed metal ion per unit mass of sorbent in mg/g, b is the Langmuir constant related to the energy of adsorption in L/mg.

The Temkin adsorption isotherm model assumes that the heat of adsorption of all the molecules in a layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that the adsorption is characterized by a uniform distribution of the bonding energies, upto some maximum binding energy[13]. The Temkin isotherm is represented by the following equation,

$$q_e = a_t + 2.3b_t \log C_e \quad (3)$$

where, q_e is the amount adsorbed at equilibrium concentration of the metal ion in mg/g, C_e is the equilibrium concentration in mg/L, a_t is the Temkin constant related to adsorption capacity in mg/g, b_t is the Temkin constant related to the intensity of adsorption in L/mg.

Adsorption kinetics: Most of the adsorption/desorption transformation process of various solid phases are time-dependent. Various kinetic models have been used by various researchers whereas, in this study, the reversible first order, pseudo-first order and pseudo-second order models were studied. Kinetic studies were carried out at different time intervals whereas concentration, carbon doses and pH are fixed.

The adsorption of ions in aqueous system follows reversible first order kinetics when a single species is considered on a heterogeneous surface[14]. The first order rate expression[15] is,

$$\ln(1 - U_t) = -kt \quad (4)$$

where,

$$U_t = \frac{C_{A(0)} - C_{A(t)}}{C_{A(0)} - C_{A(e)}} \quad (5)$$

where, U_t is the fractional attainment of equilibrium, k is the rate constant in min^{-1}, $C_{A(0)}$ is the initial concentration of Pb(II) in mg/L, $C_{A(t)}$ is the concentration of Pb(II) in mg/L present at any time 't', $C_{A(e)}$ is the concentration of Pb(II) in mg/L present at equilibrium condition.

Lagergren proposed a pseudo-first order kinetic model[16]. The pseudo-first order rate expression of Lagergren based on solid capacity is generally expressed as,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (6)$$

where, q_e is the amount of Pb(II) adsorbed at equilibrium in mg/g, q_t is the amount of metal ions adsorbed at time t in mg/g, t is the time in (min), k_1 is the pseudo-first order equilibrium rate constant in min^{-1}.

The adsorption kinetics is also described by pseudo-second order reaction[17]. The linear-integral form of pseudo second order model rate equation may be expressed as,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where, q_e is the amount of metal ions adsorbed at equilibrium in mg/g, q_t is the amount of metal ions adsorbed at time t (mg/g), t is the time (min), k_2 is the pseudo-second order adsorption rate constant (g/mg/min).

RESULTS AND DISCUSSION

Effect of pH: The effect of pH on the removal of Pb(II) with the carbon dose of 0.5 mg for the three carbons CSCAC, CNHCAC and CS-CNHCAC are shown in Fig. 1

From the figure it is clearly evident that, both the carbons CSCAC, CNHCAC and the mixed adsorbent (CS-CNHCAC) are effective for the quantitative removal of Pb(II) over the pH range 2-6. Hence, the optimum pH was fixed as 4 for CSCAC and CNHCAC for further studies. However, in the case for the mixed adsorbent (CS-CNHCAC), the optimum pH was fixed as 3.

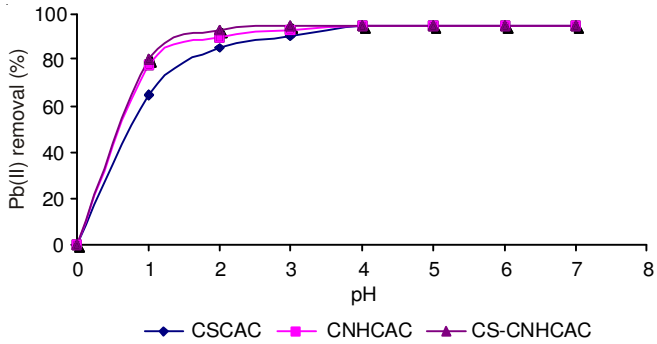

Fig. 1. Effect of pH on removal of Pb(II)

Effect of carbon dose: Fig. 2 represents the effect of carbon dose on the removal of Pb(II) at pH 4 for CSCAC and CNHCAC and at pH 3 for the mixed adsorbent CS-CNHCAC.

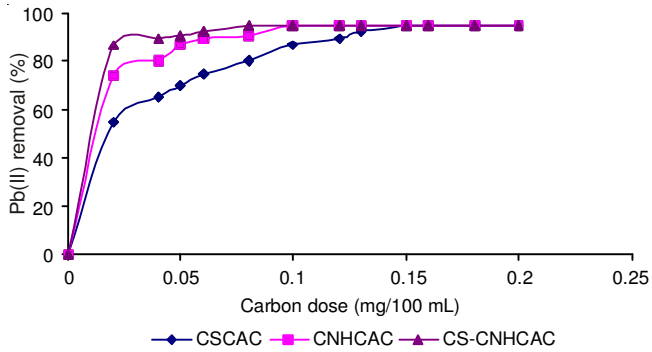

Fig. 2. Effect of carbon dose on removal of Pb(II)

For quantitative removal of Pb(II), a minimum dose of 0.15 g of CSCAC, 0.1 g of CNHCAC is required. From the Fig. 2, it is clearly evident that 0.08 g is enough for CS-CNHCAC to remove Pb(II) quantitatively.

Effect of equilibration time: Fig. 3 represents the effect of equilibration time on the removal of Pb(II) by 0.15 g of CSCAC, 0.1 g of CNHCAC and 0.08 g of CS-CNHCAC. For CSCAC an optimum time of 4 h was needed for Pb(II) removal, 3 h was enough for CNHCAC and for the mixed carbon CS-CNHCAC 2 h was required.

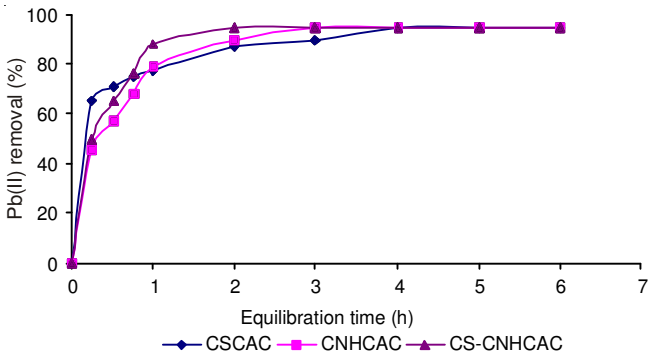

Fig. 3. Effect of equilibration time on removal of Pb(II)

From the above results of the batch studies, it is clearly evident that the mixed adsorbent (CS-CNHCAC) is the most suitable quantitative adsorbent for the removal of Pb(II) under the effect of pH, effect of carbon dose and the effect of equilibration time.

Desorption studies: Fig. 4 illustrates the effect of desorption of Pb(II) by HCl from CSCAC, CNHCAC and CS-CNHCAC. From the graph it is clearly evident that 0.2 M HCl is enough to desorb Pb(II) quantitatively from all the three carbons.

Adsorption isotherms: Plots of log (x/m) *vs.* log C_e for the Freundlich isotherm for the three adsorbents are shown in Fig. 5.

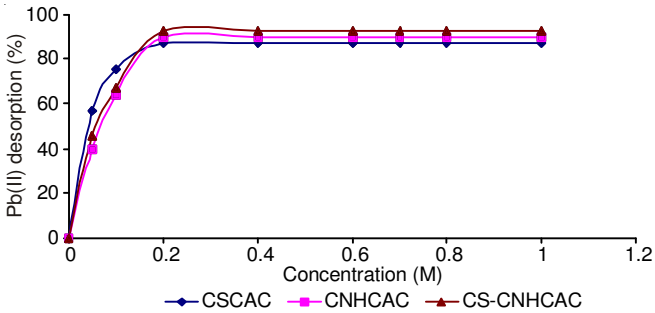

Fig. 4. Effect of concentration of acid on desorption

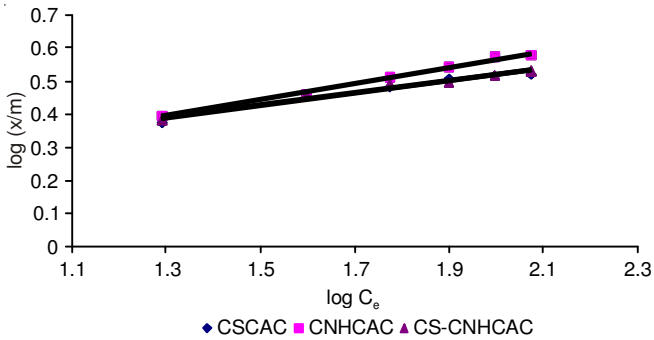

Fig. 5. Freundlich adsorption isotherm for adsorption of Pb(II)

Plot of log (x/m) *vs.* log C_e are linear for the three carbons. The straight line nature of the plots indicates that the process followed were of Freundlich adsorption type. The K_f and n values for the three carbons were calculated from the slopes and intercepts, respectively and the calculated values are tabulated in Table-2 along with the regression co-efficient (R^2) values. The values of $1 < n < 10$ showed the favourable adsorption of Pb(II) on the three carbons.

TABLE-2
FREUNDLICH ADSORPTION ISOTHERM VALUES

S. No	Carbon	K_f (mg/g)	n (L/mg)	R^2
1	CSCAC	1.3873	5.3333	0.9603
2	CNHCAC	1.2109	4.1736	0.9936
3	CS-CNHCAC	1.4352	5.5494	0.9696

The linear plots of C_e/q_e *vs.* C_e showed that the adsorption obeys Langmuir model for the three carbons as shown in Fig. 6.

The linear nature of the Langmuir plot shows that the adsorption follows the Langmuir isotherm. The Langmuir constants Q_0 and b were determined from the intercepts and slopes of the Langmuir plots. The calculated values of the Langmuir constants and the corresponding regression co-efficients (R^2) values are tabulated in Table-3.

The values of the separation parameter R_L, of the Langmuir isotherm was calculated and the calculated values of R_L for

TABLE-3
LANGMUIR ADSORPTION ISOTHERM VALUES

S. No	Carbon	Q_0 (mg/g)	b (L/mg)	R^2
1	CSCAC	3.5971	3.6614×10^{-4}	0.9998
2	CNHCAC	3.6232	3.0762×10^{-4}	0.9992
3	CS-CNHCAC	4.2918	2.0676×10^{-5}	0.9968

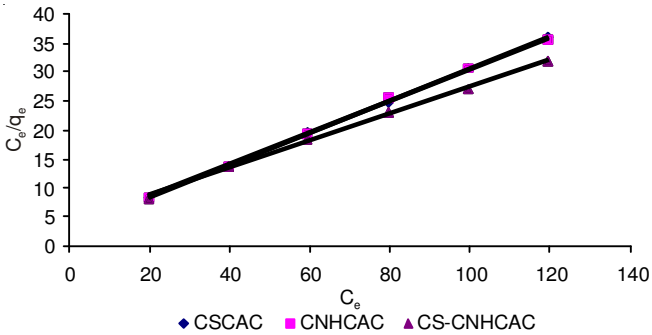

Fig. 6. Langmuir adsorption isotherm for adsorption of Pb(II)

the three carbons under different initial metal ion concentrations are tabulated in Table-4.

TABLE-4
SEPARATION PARAMETER R_L VALUES FOR THE THREE CARBON UNDER DIFFERENT INITIAL CONCENTRATIONS

S. No	C_0 (mg/L)	CSCAC	CNHCAC	CS-CNHCAC
1	20	0.9927	0.9939	0.9996
2	40	0.9856	0.9878	0.9992
3	60	0.9785	0.9819	0.9988
4	80	0.9715	0.9760	0.9983
5	100	0.9647	0.9702	0.9979
6	120	0.9579	0.9644	0.9975

The calculated separation parameter or the equilibrium parameter R_L values between 0 and 1 indicates the favourable adsorption of Pb(II) on the three carbons.

Fig. 7 shows the Temkin isotherm plot for the three carbons. The graph reveals the linear nature of the log C_e *vs.* q_e plot which shows that Temkin adsorption isotherm obeys for the different carbons.

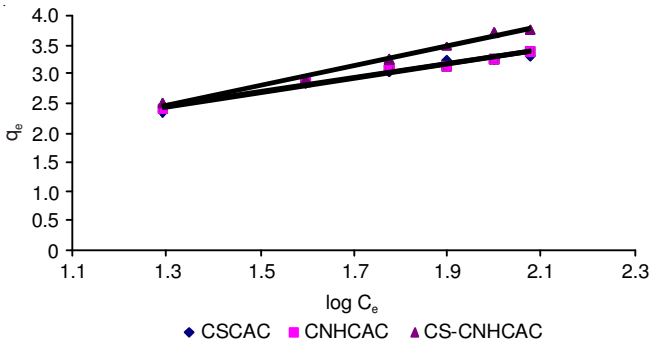

Fig. 7. Temkin adsorption isotherm for adsorption of Pb(II)

The values of the Temkin isotherm parameters are calculated from the slopes and intercepts of the Temkin plot and the calculated values are tabulated in Table-5 along with the regression co-efficient R^2 values.

On comparing the regression co-efficient (R^2) values of Freundlich, Langmuir and Temkin adsorption isotherms, to

TABLE-5
TEMKIN ADSORPTION ISOTHERM VALUES

S. No	Carbon	a_t (mg/g)	b_t (L/mg)	R^2
1	CSCAC	6.9040	0.5306	0.9739
2	CNHCAC	8.1546	0.5153	0.9816
3	CS-CNHCAC	9.6936	0.7420	0.9886

ascertain which model would be more suitable for the adsorption of Pb(II) on different carbons, it is found that the R^2 values of Langmuir adsorption isotherm are much closer to one than that of Freundlich and Temkin adsorption isotherm.

Adsorption kinetics: Kinetic studies were carried out at different time intervals whereas concentration, carbon doses and pH are fixed.

Fig. 8 shows the plot of reversible first order kinetics of Pb(II) for 20 mg/L in 100 mL. The straight line plot of ln $(1-U_t)$ *vs*. t indicates that the adsorption followed reversible first order kinetics for the three adsorbents.

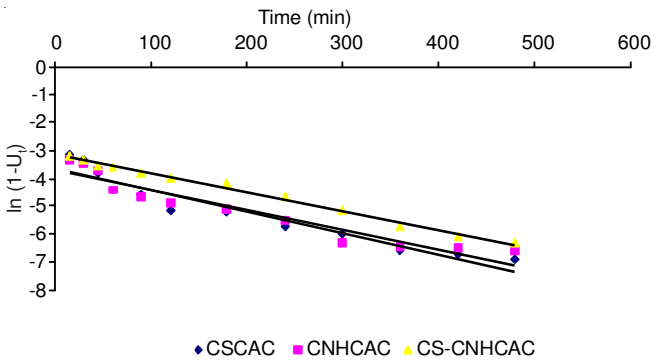

Fig. 8. Reversible first order kinetic fit of Pb(II) for 20 mg/L in 100 mL

The adsorption rate constant k along with R^2 values was calculated and presented in Table-6.

TABLE-6
ADSORPTION RATE CONSTANTS
OF REVERSIBLE FIRST ORDER KINETICS

Metal ion concentration	Carbon	$K = k_1 + k_2$ (min^{-1})	k_1(min^{-1})	k_2(min^{-1})	R^2
20 mg/L in 100 mL	CSCAC	0.0077	0.0075999	0.0001001	0.9125
	CNHCAC	0.0071	0.0070219	0.0000781	0.9052
	CS-CNHCAC	0.0068	0.0067048	0.0000952	0.9910

From Table-6, it is clear that the forward rate constant k_1 is much higher than the backward rate constant k_2 suggesting that the rate of adsorption is clearly dominant in all the three carbons for 20 mg/L in 100 mL. The applicability of reversible first order rate equation was also confirmed by their R^2 values which were near to unity.

A plot of log (q_e-q_t) *versus* time shown in the Fig. 9 for pseudo first order kinetics gives a straight line with slope of k_1 and an intercept of log q_e for 20 mg/L in 100 mL for different carbons.

The values of the rate constant k_1 were determined from the slope of the plots and are given along with the regression co-efficient R^2 are tabulated in Table-7.

The applicability of pseudo-first order rate equation was also confirmed by their R^2 values which were closer to unity.

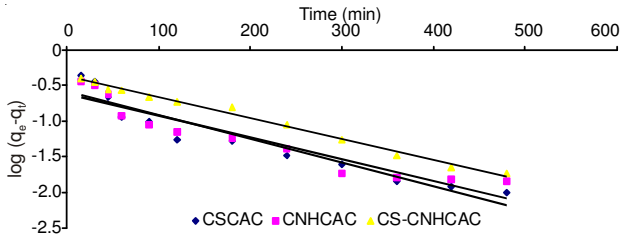

Fig. 9. Pseudo first order kinetic fit of Pb(II) for 20 mg/L in 100 mL

TABLE-7
PSEUDO FIRST ORDER KINETIC
CONSTANTS FOR THE ADSORPTION OF Pb(II)

Metal ion concentration	Carbon	q_e (mg/g)	k_1 (min^{-1})	R^2
20 mg/L in 100 mL	CSCAC	0.2602	0.0076	0.9112
	CNHCAC	0.2433	0.0071	0.9043
	CS-CNHCAC	0.4276	0.0069	0.9912

Fig. 10 shows the linear plot for pseudo second order kinetics for 20 mg/L in 100 mL for different carbons.

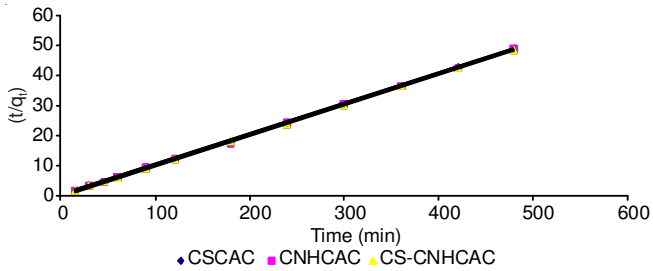

Fig. 10. Pseudo second order kinetic fit of Pb(II) for 20 mg/L in 100 mL

A plot of t/q_t *vs*. t also formed a straight line with slope of $1/q_e$ and an intercept of $1/k_2q_e^2$. The values of k_2 and q_e were determined from the slopes and intercepts of the straight line plot. The evaluated second order kinetic parameters for various carbons at 20 mg/L in 100 mL are presented in Table-8.

TABLE-8
PSEUDO SECOND ORDER KINETIC
CONSTANTS FOR THE ADSORPTION OF Pb(II)

Metal ion concentration	Carbon	q_e (mg/g)	k_2 (g/mg/min)	R^2
20 mg/L in 100 mL	CSCAC	9.8425	3.5595	0.9998
	CNHCAC	9.8814	6.8277	0.9997
	CS-CNHCAC	9.8912	6.8141	0.9999

The applicability of pseudo-second order rate equation was also confirmed by their R^2 values which were near to one for all the carbons at different metal ion concentration.

On comparing the regression coefficients R^2 values for reversible first order kinetics, pseudo-first order kinetics and pseudo-second order kinetics, it is found that R^2 values are very closer to one for pseudo-second order kinetics than the others. This result indicates that the adsorption of Pb(II) on CSCAC, CNHCAC and CS-CNHCAC is governed by pseudo-second order kinetics predominantly for 20 mg/L in 100 mL.

Conclusion

The mixed adsorbent can be successfully used for the quantitative removal of Pb(II) at optimum pH, carbon dose

and equilibration time. Desorption studies show that 0.2 M HCl is found to be suitable to desorb the Pb(II) quantitatively. Langmuir model is the most suitable model for the adsorptive removal of Pb(II) for different carbons as the regression co-efficient (R^2) values of Langmuir adsorption isotherm were much closer to 1 than that of Freundlich and Temkin models. The results of the kinetic studies revealed that the adsorption of Pb(II) on different carbons were governed by pseudo-second order kinetics predominantly. Though surface areas of the carbons are found to be lower, high adsorption capacity may be due to the presence of functional groups such as $-SO_3H$, phenolic OH as they were treated with sulphuric acid and $Na_2S_2O_8$ during preparation. As a result it is concluded that the mixed adsorbent CS-CNHCAC is used for the removal of heavy metals from industrial effluents since it is of low-cost and abundant when compared with CSCAC and CNHCAC.

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