Modelling the removal of lead from synthetic contaminated water by activated carbon from biomass of Diplocyclos Palmatus by RSM

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Abstract

Diplocyclos Palmatus biomass activated carbon (DPAC) was used in this work to remove lead (II) ion from the synthetic wastewater. The DPAC was characterized for structural, surface morphology by SEM, whereas, the functional group was analyzed by FT-IR and XRD analysis. The Removal of Pb^{2+} was studied by batch method and various experimental parameters namely effect of Pb^{2+} concentration, contact time, effect of temperature; pH and effect of matrix were also studied. The Kinetic modelling studies showed that the adsorption of Pb^{2+} ion follows pseudo second order mechanism and Langmuir isotherm model was found to fit better for this study. The Thermodynamic study showed a negative value for ΔG indicating the process was spontaneous. Box Behnken Design using response surface methodology as DOE was carried out in this work. The RSM modelling was found to be successful in predicting the removal efficiency with R^2 greater than 0.95.

Keywords: DPAC, hazardous Pb^{2+}, adsorption isotherm, kinetic models, effect of matrix, response surface methodology.

1. Introduction

Many of the organic and inorganic pollutant such as dyes and heavy metals are one of the most dangers to our environment. Electroplating, Tannin, leather industry, battery manufacturing, smelting and mining are the major sources of the discharge of lead contaminated water (Azimi *et al.*, 2017; Xu *et al.*, 2017) to the environment. Among the trace metals, Cu^{2+}, Pb^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+}, Cr^{2+}, Ni^{2+} and As^{2+} have been considered as pollutants in the contaminated water. If the Lead was taken in small amount, it heavily injures the human body, affecting the central brain, kidney and liver. The central nervous system disorders causes coma and death. Also, the Lead poisoning in lower concentration may lead to anaemia and produce blue line on gums (Davies *et al.*, 2016). There were two methods used for the removal of heavy metals viz., conventional and non conventional methods (Fu *et al.*, 2016). The natural materials used for the elimination of trace metals from the contaminated water includes agricultural waste, coir pith, bone chair, wool, silk, and human hair (ATSDR, 2007). From the literature review, the activated carbon were readily available and cheap from the materials such as rice husk, fly ash, peanut husk and cow dung which were used for the removal of heavy metals from the contaminated water (Brown, 2012; Tong *et al.*, 2000; Jia Guo *et al.*, 2000). The Microwave radiation which was used to heat dielectric materials was also used to prepare activated carbon from various sources. The main advantage of using the microwave activation is that the treatment time would be considerably reduced; reduction in the energy consumption and also gases evolved in the treatment could also be reduced. Microwave activation can be done by both internal and volumetric heating for the preparation of activated carbon (Li *et al.*, 2009). Therefore, microwave induced activation was rapid and effective at a lower temperature, resulting in the reduced treatment time (Venkatesh and Raghavan, 2004). Microwave heating technique have additional applications such as interior heating, higher heating rate, selective heating, controllable heating process. There was no direct contact with the heating source and materials and also it reduced the consumption of time (Liu *et al.*, 2013). The RSM methodology was used to find out the best combination of various factors which control the removal of Pb^{2+} from the wastewater. RSM simplified the number of experiments and decreased the cost, reduced the experimental problems and needed less time compared to other statistical methods (Shahrak *et al.*, 2016). Box Behnken Design (BBD) was used in this work for modelling and predicting the removal of Pb^{2+} ion by DPAC and the factors involved in the study were the concentration of Pb^{2+} ion, time of contact temperature and time. RSM was chosen as a compelling statistical and scientific approach so as to distinguish the efficiency of experimental method. Different parameters were applied in RSM at the same time to get a few numbers of experiments by the Design of Experiment (DOE). In the present study, the biomass of Diplocyclos Palmatus was

used to prepare activated carbon as adsorbent to remove heavy metal particularly Pb^{2+} ion from synthetic water. The biomass of Diplocyclos Palmatus activated carbon (DPAC) has not been reported in the literatures to our best knowledge and this is a novel work.

2.   Experimental

2.1. Materials

The biomass of Diplocyclos Palmatus was collected from shevaroy hills. The materials were dried for 3 days in air without exposure to sunlight and then crushed into fine size. The stems were then powered and sieved. The sieved samples were taken into chemical activation.

2.2. Adsorbent preparation and characterization

The sieved sample of Diplocyclos Palmatus biomass were mixed with 50 % of phosphoric acid in 1:1 ratio and heated in the fume hood without stirring for 48 hours for complete dehydration. The liquid portion was then carefully decanted and the remaining solid portion was then taken in a stainless steel autoclave reactor. The autoclave reactor was heated in microwave oven with a constant N_2 flow of 150 m^3/min at 120^oC for 2 hours. After the heating process the activated carbon was cooled under N_2 atmosphere and then washed with distilled water to neutral pH. The activated carbon (DPAC) was then dried at 100^oC for 1 hour in air oven. DPAC and Pb^{2+} loaded DPAC surface morphology was carried out using the scanning electron microscope-EDS (Tescan Brno 62300) instrument. The FT-IR of both the samples were taken to characterize the functional group after and before the adsorption using Perkin Elmer spectrophotometer. The Atomic Absorption spectrophotometer (Systronic, India SL 163) was used to determine the concentration of the Pb^{2+} ion before and after adsorption in the solution. AAS analysis was done in triplicate and average results were used in this study to reduce the error in analysis.

2.3. Synthesis of adsorbate solution

1.5984 g of $Pb(NO_3)_2$ was dissolved in 1000 mL of double distilled water to give a concentration of 1000 mg L^{-1} of Pb^{2+} ion in solution. From the 1000 mg L^{-1} stock solution, 10 mL was diluted to 100 mL which gives 100 mg L^{-1} (100 ppm) working solution. Experimental solutions of desired concentration were then obtained by successive dilutions. The initial pH measurements were carried out by pH instrument and were calibrated using the buffer solutions of pH values. The pH of the synthetic contaminated water was adjusted by the addition of diluted HCl and NaOH solutions.

3.   Characterization of the adsorbent

3.1. Surface morphology of the adsorbent

The surface morphology of the adsorbent was characterized by SEM with EDS. The scanning electron microscope image of the adsorbent and Pb^{2+} loaded carbon were shown in Figure 1(a, c). The SEM images clearly differentiated the effect of the particle size of the DPAC. DPAC has excellent pore size, and the particles have high porosity, large surface area which gave a high solid surface, resulting in the efficiency of trace metals' removal from the contaminated water. From the Figure 1(b, d) the EDS image of DPAC before and after adsorption of the Pb^{2+} onto the DPAC were shown. The DPAC consisted of carbon, oxygen, silicon and traces of calcium. The Presence of silicon was common in the bark of the plants and in Figure 1(d), the presence of the Pb^{2+} ion which was due to the adsorption of the metal onto the activated carbon was shown.
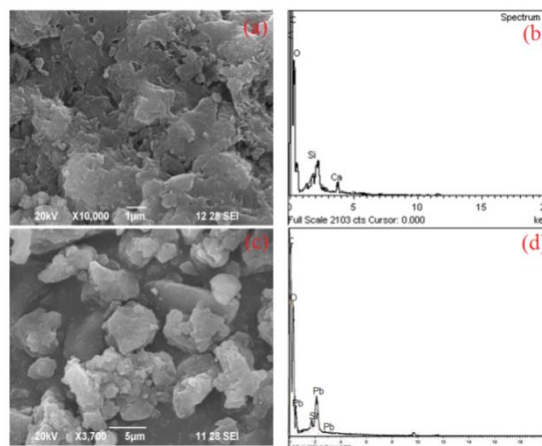

Figure 1. SEM-EDS images (a, b) shows the pure biomass of the DPAC, (c, d) show the after adsorption Pb^{2+} onto the biomass of the DPAC

3.2. Functional group analysis

Fourier transform infrared spectroscopy was used to investigate the functional group in the DPAC and metal ion adsorbed activated carbon which were shown in Figure 2 (a, b). The spectrum of the DPAC before and after adsorption clearly showed a change in the nature of the peak, its intensity and the wave number. The FT-IR spectrum clearly suggested that the functional group in the activated carbon has played an important role in binding the Pb^{2+} ion in the solution. The spectra of DPAC showed a broad peak at around 3500 to 3000 cm^{-1} indicating the presence of OH group from the hydroxyl and carboxyl functional group. The peak around 2900 cm^{-1} suggested the presence of amine group. The broad peak around 1700 cm^{-1} suggested the presence of C=O group in the DPAC. The peak at 1300 cm^{-1} were assigned to methyl and methylene C-H bending vibration.

XRD spectrum of DPAC was presented in Figure (3). From the XRD, it can be seen that there was no characteristic sharp peak which indicated that the carbon was amorphous in nature. A broad peak at $2\theta = 15$-$30°$ was due to the partial graphitization of the carbon in the DPAC. It can be concluded from the XRD that the complete activation of the carbon has occurred with a very little crystallization still present in the DPAC.

4.   Batch adsorption method

Batch studies were performed in a closed plastic container (250 ml capacity) with 100 ml of adsorbate solution of

different concentration ranging from 5 mg L^{-1} to 200 mg L^{-1}. Constant shaking of the solution was done using mechanical orbital shaker at the rate of 150 rpm. The ambient temperature was maintained throughout the experiment. The sample was shaken for 1 hour and then the sample was collected and filtered as discussed earlier.
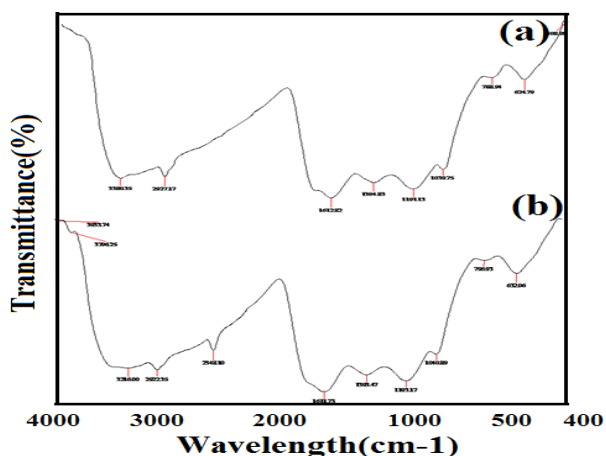

Figure 2. FT-IR image (a, b) shows the before and after adsorption of Pb^{2+} onto the biomass of DPAC
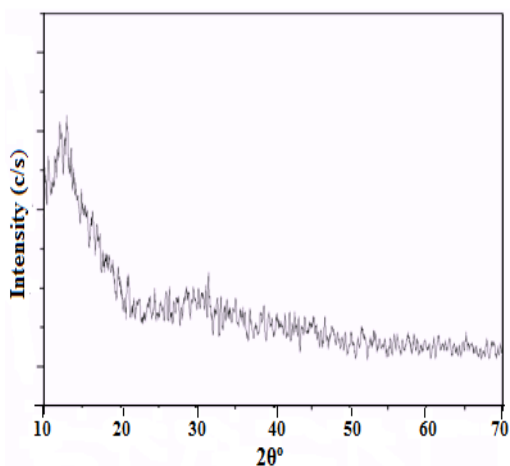

Figure 3. XRD image show the biomass of DPAC

The removal efficiency of the Pb^{2+} by the activated carbon was expressed by

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

Where C$_o$ and C$_e$ is the initial and equilibrium concentration in mg L^{-1} of the Lead in water.

5. Results and discussion

5.1.1. Effect of concentration

The % removal of the Pb^{2+} by the DPAC with various concentrations of lead ion was showed in Figure 4(a). With an increase in the concentration of Pb^{2+}, it has been found that the removal % decreases. The % removal of the Pb^{2+} was fairly constant up to 60 mg L^{-1} with around 85 % and decreased afterward. The decrease in the % removal of the Pb^{2+} can be attributed to the fact that the surface of the adsorbent might have been fully saturated. The higher

concentration of Pb^{2+} showed much less removal % with 60 mg L^{-1} solution which showed a removal percentage of 85.76 %, then 100 mg L^{-1} solution gave a 60.92 % removal and 200 mg L^{-1} solution gave 32.05 % removal. In terms of the amount of Pb^{2+} adsorbed by the DPAC, the maximum amount of the Pb^{2+} adsorbed was found to be 60.92 mg g^{-1}. The maximum amount of the Pb^{2+} removal in terms of the mass of Pb^{2+} was shown by the solution of 200 mg L^{-1}. The solution of 200 mg L^{-1} showed a maximum removal of 64.11 mg g^{-1}. The decrease in the percentage of Pb^{2+} adsorption by 200 mg L^{-1} solution may be attributed to the fact that at equilibrium condition there might be more of the desorption taken place rather than adsorption. 60 mg L^{-1}, 50 mg L^{-1}, 40 mg L^{-1} and 30 mg L^{-1} solution showed a maximum removal of 51.46 mg g^{-1}, 43 mg g^{-1}, 39.65 mg g^{-1} and 25.34 mg g^{-1} respectively. So with an increase in the concentration, it was seen that the surface coverage was increased and the removal reached a saturation point at around 60 mg L^{-1}.

5.1.2. Effect of time of contact

The effect of the contact time on the percentage of removal of Pb^{2+} by the DPAC was also shown in Figure 4(a). The Time effect was studied by shaking the Pb^{2+} solution with activated carbon for a specified time interval. Various time intervals were chosen for determining the removal of the Pb^{2+} by the DPAC. 10, 20, 30, 40, 50 and 60 minutes with the time interval of 10 minutes were taken up for the studies. After that 75, 90, 120 and 240 minutes were taken for the removal of Pb^{2+} by the DPAC. It is a known fact that with an increase in the contact time there would be an increase in the adsorption because with the higher time of contact there would be higher amount of adsorption taking place. DPAC showed a maximum removal of the Pb^{2+} occurs at an interval of 10 minutes itself, with a removal percentage of 62.4 %, which suggested that the adsorption takes place at quicker pace initially with many pore sites available in the activated carbon. With increase in the time the adsorption became slower, with 91.6 % of the adsorption being completed at an interval of 30 minutes itself. The higher rate of adsorption showed the spontaneous effect of the adsorption at initial stages and equilibrium was reached after 30 minutes. With a further increase in the time, the percentage removal remains fairly constant. Pb^{2+} adsorption in the activated carbon attain equilibrium in 30 minutes and further increase in time of contact does not have any effect on the removal of the Pb^{2+} by the DPAC.

5.1.3. Effect of temperature

The temperature effect can be taken as the indicator to determine whether the adsorption was physical adsorption or chemical adsorption. In this study from Figure 4(c), it can be seen that the DPAC showed a decrease in adsorption of Pb^{2+} with an increase in temperature. This clearly showed that physical adsorption was the main process which controlled the mechanism of Pb^{2+} ion adsorption into an activated carbon. At lower temperature the maximum removal of the Pb^{2+} was found to be 98 % for 10 mg L^{-1} solution. For the temperature

35°C, the maximum removal was 97.5 % for 10 mg L^{-1} solution and the removal efficiency drastically decreased with increase in concentration of the solution. The removal % was 95.8 %, 93.7 %, 89 % for the temperatures 45°C, 55°C, 65°C respectively. For all the temperatures, the higher concentration showed lower removal with minimum removal efficiency in 200 mg L^{-1} solution.
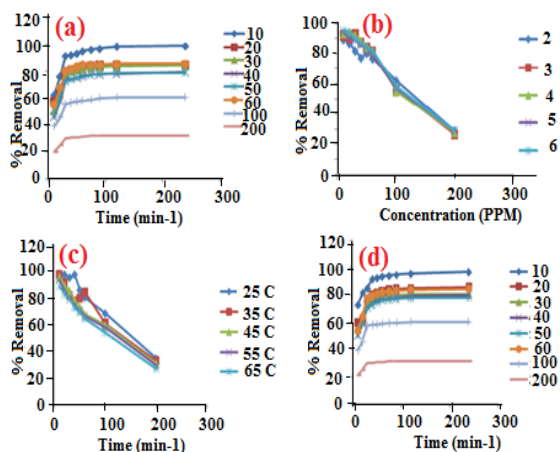

Figure 4. (a, b, c, d) Removal % of Pb^{2+} by DPAC at different concentration, pH, temperature, and contact time

5.1.4. Effect of matrix

Industrial wastewater may contain many other ions present along with the Pb^{2+} which may affect the adsorption of the Pb^{2+} in DPAC. So, in this study, the effect of other ions on the adsorption of the Pb^{2+} in DPAC at different concentrations of the Pb^{2+} prepared in 1 % Na$_2$SO$_4$, 1 % NaNO$_3$ and 1 % NaCl was studied. These salts were chosen because most of the industrial water was having a higher percentage of SO$_4^{2-}$, NO$_3^-$, and Cl$^-$. The removal % was 95.7 % 96.5 %, and 97.6 % for NaCl, Na$_2$SO$_4$ and NaNO$_3$ respectively in 10 mgL^{-1} Pb^{2+} ion concentration.

5.1.5. Effect of pH on Pb (II) adsorption

Aqueous phase pH governed the measurement of heavy metal and also the dissociation of active functional sites on the adsorbent. Hence, the metal adsorption was critically correlated with pH. Different metals showed different pH optima for their adsorption and also varied with the surface functional group. The surface property of the activated carbon depends on the pH of the system which in turn determines the form in which lead (II) ion could exist. It was observed that the maximum adsorption occurred at pH 6. Almost 96 % of Pb^{2+} removal was observed at this pH at 100 mg L^{-1} Pb^{2+} concentration. The pH of the solution has a profound effect on the removal of the Pb^{2+} from the adsorbent. The existence of the particular oxidation state in the environment depends on the pH of the solution in which the particular metal was present. Some metal would get precipitated at certain pH. For this

study, the pH range was taken from 2 to 6. This particular pH range was taken because at higher (pH > 6) Pb^{2+} would get precipitated as Pb(OH)$_2$ and the removal of the Pb^{2+} was not possible.

5.2. Thermodynamic study

The standard Gibb's energy was evaluated by

$$\Delta G° = -RTlnK_c \tag{2}$$

Where R ideal gas constant (R = 8.314 J mol^{-1} K^{-1}) and T is the temperature (K).

The apparent equilibrium constant (K$_c$) of the adsorption is defined as:

$$Kc = \frac{C_{ad.eq}}{C_{eq}} \tag{3}$$

C$_{ad}$, equilibrium and C$_{eq}$ were the concentrations of Pb^{2+} on the adsorbent and at equilibrium respectively. The standard thermodynamic equilibrium constant (K$_c$) can be used to determine the enthalpy and entropy of the system.

$$lnK_c = -\frac{\Delta G°}{RT} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{RT} \tag{4}$$

The plot of ln K$_c$ as a function of 1/T yields on shown Figure 5, a straight line from which ΔH° and ΔS° can be calculated from the slope and intercept, respectively and were presented in Table 1.

Table 1. Thermodynamic parameters of adsorbent at initial concentration of 50 mg L^{-1}

Temp (K)	ΔG° (K J mol^{-1})	ΔH° (K J mol^{-1})	ΔS° (K J mol^{-1}K^{-1})
308	-3.52437		
318	-2.67813	-10.7417	-25.5988
328	-2.40736		
338	-2.31442		

From the Table 1 -ΔG° at all temperatures were negative which indicated the spontaneous nature of the adsorption of Pb^{2+} in DPAC. The change of the standard free energy increased with increasing temperatures which indicated that a better adsorption was actually obtained at lower temperatures. Moreover, the standard free energy change for multilayer adsorption was more than −20 kJ mol^{-1} and less than zero. It should be noted that the magnitude of ΔG° values was in the range of multilayer adsorption. Negative ΔH° showed the exothermic nature of adsorption and negative ΔS° showed the decreased randomness at the solid/solution interface during the adsorption process. This suggested that Pb^{2+} ions replace some water molecules from the solution which was previously adsorbed on the surface of the adsorbent. The values of ΔH° and ΔG° suggested that physisorption have taken place between the Pb^{2+} ions and DPAC at all temperature. These displaced molecules gained less translation entropy, thus allowing the prevalence of randomness in the system. Table 1 summarized the values of these thermodynamic properties.

5.3. Adsorption isotherms

The successful illustration of the dynamic adsorptive separation of solute from solution in an adsorbent depends upon a good description of the equilibrium separation between the two phases. An adsorption isotherm was characterized by certain constant values, which expressed the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. In order to determine the mechanism of Pb^{2+} adsorption in the activated carbon and evaluate the relationship between adsorption temperatures, the experimental data was applied to the Langmuir and Freundlich isotherm equations. The adsorption isotherm constant (Q_0, B, K, n) parameters were calculated by a linear regression form of the isotherm equations. The constant parameters and correlation coefficient (R^2) were summarized in Table 2.

Langmuir isotherm model

$$\frac{C_e}{qe} = \frac{1}{bK} + \frac{C_e}{Q_o} \tag{5}$$

Where, C_e is the concentration at equilibrium (mg L^{-1}), q_e is the adsorption equilibrium (mg g^{-1}), Q_0 and K is the Langmuir constants related to adsorption capacity and Energy of adsorption. Freundlich isotherm model

$$q_e = K_f \, C_e^n \tag{6}$$

K_f and n is the Freundlich model constants.

Table 2. Adsorption isotherm constants for Pb^{2+} onto the DPAC

Temp (K)	Langmuir Isotherm			Freundlich Isotherm		
	Qo (mg g^{-1})	B (L g^{-1})	R^2	K (L g^{-1})	n	R^2
308	71.42	0.01	0.99	0.97	0.32	0.91
318	66.66	0.001	0.99	1.03	0.34	0.96
328	62.51	0.021	0.99	1.10	0.37	0.94
338	58.82	0.016	0.99	1.16	0.38	0.92

Table 3. A comparison of the pseudo-first and second order model rate constants and theoretical (the) and experimental (exp) q_e values were obtained at different initial Pb^{2+} concentrations and temperatures

Temp (^{0}C)	C_o (mg L^{-1})	Exp q_e (mg g^{-1})	Pseudo-first order			Pseudo-second order			
			k_1 (min^{-1})	the q_e	R^2	K (g mg^{-1} min^{-1})	the q_e	h (mg g^{-1} min^{-1})	R^2
35	10	9.750	0.082	-27.77	0.95	0.0418	9.900	4.098	0.99
	50	39.92	0.096	-23.80	0.96	0.0055	41.66	9.708	0.99
	100	60.87	0.032	-71.42	0.36	0.0036	62.50	14.28	0.99
	200	65.75	0.112	-21.01	0.90	0.0034	71.42	17.54	0.99
45	10	9.580	0.055	-41.66	0.97	0.0278	9.803	2.673	1
	50	36.68	0.105	-21.73	0.91	0.0073	38.46	10.86	0.99
	100	59.43	0.108	-21.27	0.94	0.0037	62.50	14.70	0.99
	200	61.67	0.110	-20.83	0.91	0.0062	60.60	24.39	0.99
55	10	9.370	0.089	-25.64	0.97	0.0508	9.523	4.608	0.99
	50	35.37	0.644	-35.71	0.87	0.0082	37.03	11.36	0.99
	100	57.82	0.112	-20.40	-0.04	0.0049	58.82	17.24	0.99
	200	58.86	0.136	-22.22	0.83	0.0095	62.50	23.25	0.99
65	10	8.900	0.736	-31.25	0.86	0.0330	9.090	2.732	1
	50	34.75	0.967	-23.80	0.86	0.0087	35.71	11.11	0.99
	100	54.26	0.113	-22.72	0.87	0.0055	55.55	17.24	0.99
	200	53.98	0.089	-25.64	0.71	0.0076	54.05	22.22	0.99

As seen Table 2, Langmuir and Freundlich isotherms of Pb^{2+} adsorption on surface DPAC were found to be linear over the whole temperature range studied and R^2 was extremely high. The value of Q_o decreased with the increase in temperature, thereby confirming that the process was exothermic (Fountouli and Chrysikopoulos, 2018). It indicated that Pb^{2+} was favourably adsorbed by the DPAC. The values of K and n determined from the Freundlich model changed with the rise in temperature. The magnitude of K showed a low Pb^{2+} adsorptive capacity of the DPAC from aqueous solution at all temperature (K). Table 2 also indicated that n was less than 1.0 at all temperatures, indicating that Pb^{2+} was unfavourably adsorbed by DPAC.

5.4. Adsorption kinetics

Kinetics of the adsorption of lead in DPAC was monitored using pseudo-first order and pseudo-second order rate equation which can be represented

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{7}$$

Amount of the metal ion adsorbed at time t was given by q_t (mg g^{-1}) and first order rate constant was given by k_1

(min^{-1}). A straight line of log (q_e – q_t) vs t suggested the applicability of this kinetic model. q_e and k_1 could be calculated from the intercept and slope of the plot, respectively.

The pseudo-second order kinetic model (H_o equation) is expressed as

$$\frac{1}{q_t} = \frac{1}{K_2 q_q^2} + \frac{1}{q_e}t \tag{8}$$

Where, k_2 is the rate constant of second order adsorbent. The plot t/q_t versus t should have been a straight line if pseudo-second-order kinetics was applicable whereas, the slope and intercept of the plot would give q_e and k_2, respectively.

$$h = K_2 q_e^2 \tag{9}$$

Where h is the initial sorption rate

Table 3 provides the values of pseudo-first order rate constants k_1, pseudo-second order rate constants k_2, h, calculated equilibrium sorption capacity q_e, the (theoretical) and experimental equilibrium sorption capacity q_e, exp (experimental) at various initial Pb^{2+} concentrations and temperatures. The validity of the kinetic models was tested by the magnitude of the regression coefficient R^2 as given in Table 3. It is important to note that for a pseudo-first order model, the correlation coefficient was always less than 0.97, on the other hand, the application of a pseudo-second order model lead to much better regression coefficients, all values equal to or greater than 0.99. Moreover, the values of the q_e, estimated from the first order kinetic model gave significantly different values compared to exp q_e values and were found to be fairly lower. However, in pseudo-second order kinetic model, the q_e values (the) were very close to q_e values (exp) at various initial Pb^{2+} concentrations and temperatures. The pseudo-second order model has been found to be extensively applied for studying physiochemical interaction in numerous environmental adsorption studies (Sotirelis and Chrysikopoulos, 2015; Vasiliadou and Chrysikopoulos, 2011; Fountouli and Chrysikopoulos, 2018). For the pseudo-second order model, the rate constant decreased with an increase of initial Pb^{2+} concentration, while the initial sorption rate, h, generally increased with an increase of initial Pb^{2+} concentration at all temperatures. Further, the values of correlation coefficients (R^2) of pseudo-first order model were lower than those of a pseudo-second order model for all the sorption processes indicating that pseudo-second order model was better obeyed than pseudo- first order model equation. The analysis of kinetic data by other researchers showed that the pseudo-second order rate equation was a reasonably good fit for Pb^{2+} adsorption (Kose et al., 2011; Niu et al., 2016). The pseudo-second order equation provided the best correlation (R^2 = 0.99) for all of the sorption process.

5.5. Response surface methodology (RSM)

RSM is widely used for predicting and optimizing the condition for the removal of Pb^{2+} from the wastewater.

For the removal of heavy metal from wastewater, various factors like concentration of the Pb^{2+} ion, amount of adsorbent, temperature, pH and time of contact influence the process. It was hard to determine the optimal condition for each variable (factor) for the removal of Pb^{2+} since it would involve large number of experiments. But, RSM was simplified by the Design of Experiment (DOE) and if these experiments were carried out, the response would be used for determining the best combination of factor for the optimal removal of the heavy metal. In this study, Box Behnken Design (BBD) was used. The removal of pb^{2+} from the wastewater was strongly dependant on the pH. In alkaline condition, pH greater than 7, lead got precipitated from the solution hence its removal from the water was not possible at higher pH. The Central Composite Design (CCD) would involve the use of extreme condition (upper and lower limits) of pH and hence, CCD was not used in this work. The number of variables used in this work was 4 viz., concentration of the lead, contact time, pH and temperature. The Total Number of Experiments (TNE) used in this work was 27 which is according to the equation (10)

$$\text{TNE} = 2k(k-1) + C_o \tag{10}$$

Where, k = 4 is the number of variable and C_o = 3 is the number of central point in this work. Minitab 17 was used in this study for RSM study and a quadratic equation was generated according to the equation (11)

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 + \beta_{23} X_2 X_3 + \beta_{34} X_3 X_4 + \beta_{41} X_1 X_4 + \beta_{13} X_1 X_3 + \beta_{24} X_2 X_4 \tag{11}$$

X_1, X_2, X_3 and X_4 are the initial concentrations of lead (X_1), time of contact (X_2), temperature (X_3) and pH (X_4) of the solution respectively. β_0 is a constant and β'_s is the coefficient of the linear, quadratic and crossed variables.

Table 4. The values of variable for the BBD design of experiment

Parameters	Code	-1	0	+1
Concentration of dye	X_1	30	35	40
Time of contact	X_2	70	87.5	100
Temperature	X_3	40	45	50
pH	X_4	5.0	5.5	6.0

Batch run were carried out to determine the interaction between the X_1, X_2, X_3, and X_4. The results of the experiments for the removal efficiency were summarized in Table 5. The results were used to develop a regression model and a second order polynomial equation was developed (eq-11) (Amini and Younesi, 2009; Azila et al., 2008; Bingol et al., 2012). The 27 experiments were carried out and the summary of the lack of fit and analysis of variance (ANNOVA) was presented in Table 6.

$$\begin{aligned} \% \text{ Removal} = {} & 87 + 6.62 X_1 - 2.73 X_2\ 2.54 X_3 - \\ & 23.2 X_4 - 0.044 X_1 X_1 + 0.017 X_2 X_2 - \\ & 0.02 X_3 X_3 + 2.76 X_4 X_4 - 0.0093 X_1 X_2 + 0.0082 X_1 X_3 - \\ & 0.702 X_1 X_4 + 0.0115 X_2 X_3 - 0.055 X_2 X_4 + 0.62 X_3 X_4 \end{aligned} \tag{12}$$

Equation 12 can be used to predict the removal % of the Pb^{2+} from the waste water by DPAC. The sign of the

coefficient in each variable indicated whether the factor was synergistic or antagonist. The positive values of the factor indicated the synergistic effect and a negative sign of the coefficient which means it has antagonist effect. The suitability of model can be inferred by the Fishcer's 'F' test and student 't' test. The 't' test was used to determine the value of P (level of significance). In this work, F value was found to be 16.40 which was high indicating that the model was suitable for the removal of Pb^{2+} by DPAC. $P < 0.0001$ confirmed that the BBD model fits the experimental data and suitability of the statistical analysis for this work. The P value can also be used to determine the level of significance of each variable and among the variables. In this work 5 % level of significance was followed. The Linear, quadratic and interaction effect was found to be significant when $p < 0.05$. On comparing the values of lack of fit (2.165) and P (0.008) (lesser than 0.05) indicated that the lack of fit was insignificant. The non significant lack of fit indicated a good predictability of the data in this study. Correlation coefficient (R^2) was found to be high ($R^2 = 0.97$) indicating that prediction through this model has a very low error. The R^2 indicated that the model showed only 3 % error which was within the experimental limit. Figure 8 showed the linear plot of experimental and predicted value of the removal of Pb^{2+} in RSM modelling. The F statistics for linear and quadratic interaction were higher indicating that the data of each component was significant for the testing hypothesis on the factor in the model. The associated "P" value for these interactions was found to be lesser than 0.05 confirming their significance to the modelling. The 2 way interaction showed higher "P" value (0.108) suggesting that it has less significance to the model, but it was interesting to note that out of six, 2 two way interaction showed higher significance with P value less than 0.05. So it can be concluded that four 2 way interaction viz., $X_1 X_2$, $X_1 X_3$, $X_2 X_3$ and $X_2 X_4$ does not show any significance indicating that these factors does not depend on one another and hence were independent to each other. Table 6 shows that X_1, X_2, X_3 and X_4 has P values less than 0.05 were significant. X_2^2 was found to be significant in the quadratic single factor and in the quadratic two factor interaction, $X_1 X_4$ and $X_3 X_4$ were found to have $P < 0.05$ showing significance to the model.
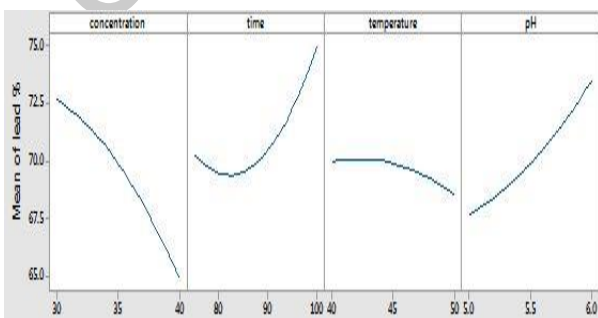
Table 5. Summarize the removal efficiency of the Pb^{2+}

| Exp. No	X_1	X_2	X_3	X_4	% removal
1	35	87.5	45	5.5	69.95
2	30	100	45	5.5	77.34
3	30	87.5	50	5.5	70.87
4	35	87.5	50	5	64.67
5	40	100	45	5.5	68.89
6	35	87.5	40	6	71.80
7	40	87.5	45	5	63.79
8	40	87.5	50	5.5	63.89
9	35	75	45	6	74.56
10	35	100	45	5	73.68
11	35	87.5	50	6	74.66
12	35	100	45	6	77.98
13	35	87.5	45	5.5	69.74
14	30	75	45	5.5	72.67
15	35	100	40	5.5	74.89
16	35	87.5	40	5	68.05
17	35	100	50	5.5	74.87
18	40	87.5	45	6	65.99
19	30	87.5	45	5	68.76
20	40	87.5	40	5.5	65.98
21	30	87.5	40	5.5	73.78
22	35	75	45	5	68.88
23	35	75	40	5.5	69.78
24	30	87.5	45	6	77.98
25	35	75	50	5.5	66.87
26	40	75	45	5.5	66.56
27	35	87.5	45	5.5	69.98
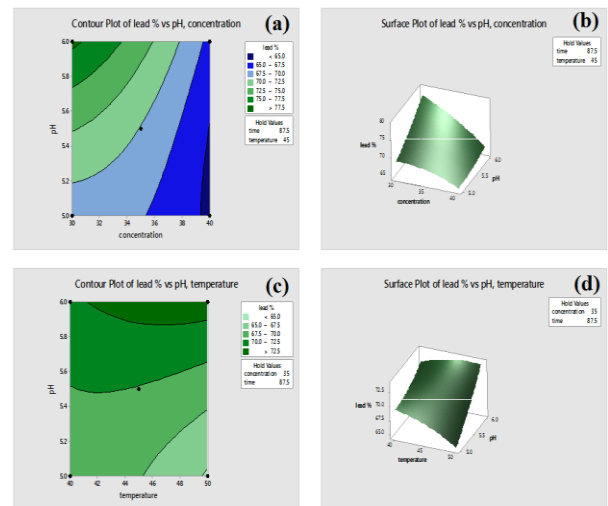
Figure 6. (a, b) Counter and surface plot of the % Pb^{2+}, pH Vs Concentration, (c, d) Counter and surface plot of the % Pb^{2+}, pH Vs Temperature

The contour plot and surface plot of the 2-way interaction which showed high significance was shown in the Figure 6. The pH was one of the most important factors for the adsorption of the lead in the activated carbon. From the contour plots, it can be inferred that lower pH resulted in lower removal of the Pb^{2+} with temperature and concentration. This can be attributed to the fact that at lower pH the functional group in the DPAC would be

Figure 5. Main effect plot of various factors on the removal of the Pb^{2+} by the DPAC

protonated resulting in the repulsion between the adsorbent and the metal.

Table 6. Summary of analysis of variance (ANNOVA)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	414.85	29.63	16.40	0.00
Linear	4	327.55	81.88	45.32	0.00
X_1	1	156.25	156.2	86.48	0.00
X_2	1	60.211	60.21	33.32	0.00
X_3	1	8.3350	8.335	4.61	0.05
X_4	1	102.75	102.7	56.87	0.00
Square	4	62.338	15.58	8.63	0.00
$X_1 X_1$	1	6.3720	6.372	3.53	0.08
$X_2 X_2$	1	33.991	33.99	18.81	0.00
$X_3 X_3$	1	1.1300	1.130	0.63	0.44
$X_4 X_4$	1	2.5050	2.505	1.39	0.26
2-Way Interaction	6	24.969	4.162	2.30	0.10
$X_1 X_2$	1	0.1980	0.198	0.11	0.74
$X_1 X_3$	1	0.1320	0.132	0.07	0.79
$X_1 X_4$	1	12.327	12.32	6.82	0.02
$X_2 X_3$	1	2.0880	2.088	1.16	0.30
$X_2 X_4$	1	0.4760	0.476	0.26	0.61
$X_3 X_4$	1	9.7480	9.748	5.40	0.03
Error	12	21.683	1.807	-	-
Lack-of-Fit	10	21.649	2.165	128.7	0.008
Pure Error	2	0.0340	0.01	-	-
Total	26	436.54	-	-	-

The optimal condition for the removal of Pb^{2+} from the RSM was as follows: $X_1 = 30$ mg L^{-1}; $X_2 = 100$ min; $X_3 = 50\,^oC$; $X_4 = 6$; Predicted = 84.05 %; Experiment = 83.12%

6. Conclusion

A reactor can be designed to study the removal of the Pb^{2+} from industrial wastewater since the time required for the removal was minimum. The pH has profound effect on the removal of the Pb^{2+} from the solution. It was found that slightly alkaline pH was the ideal condition for the removal of the Pb^{2+} from the water by DPAC. The Matrix effect was found to be minimum in the removal of the Pb^{2+} from the surface modified DPAC. Langmuir model provides better correlation coefficient (R^2 = 0.99) than the Freundlich (R^2 = 0.96) model. The results indicated that the pseudo-second order equation provided the best R^2 for the adsorption. These results demonstrated the great potential of plant residues, as low-cost heavy metal adsorbed adsorbent. The heavy metal removal technique using such adsorbent would be an effective method for the economic treatment of wastewater. RSM model was successfully applied in this study and was found to predict the adsorption pretty accurately.

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