Adsorption of Pb (II) from Aqueous Solution onto Microwave Assisted Activated Carbon Prepared from Orange Peel

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ABSTRACT

Microwave assisted activated carbon produced from orange peel was used as adsorbent to remove lead ion from aqueous solution through batch adsorption. The ability of orange peel to remove lead (II) ions from aqueous solutions by adsorption has been studied under several conditions such as pH, contact time, adsorbent dose, initial concentration of lead (II) ion and temperature. The models of Langmuir and Freundlich were applied to describe adsorption equilibrium. Kinetics data were fitted by pseudo-first-order and pseudo-second-order models. The results show that the equilibrium data follow Langmuir isotherm and the kinetic data follow pseudo-second-order model. Thermodynamic parameters ($\Delta G°$, $\Delta S°$ and $\Delta H°$) for adsorption system were determined at 30°C. The results show that the Microwave assisted activated carbon prepared from orange peel can be used for the removal of lead from aqueous solutions as a low cost adsorbent.

Key words: Orange peel, heavy metal ion, adsorption, isotherms, kinetics.

1. Introduction

The excessive release of heavy metals into the environment is a major concern worldwide. Lead contamination in drinking water is a major source of concern due to its detrimental effect on human health when ingested, its pollution results from textile dyeing, ceramic and glass industries, petroleum refining, battery manufacture and mining operations. Various processes of heavy metals elimination, in particular lead, are used, we can cite: precipitation, electro precipitation, electro coagulation, cementing and separation by membrane, the solvent extraction and the exchange of ions on resins. Strict environmental protection legislation and public environmental concerns lead the search for novel techniques to remove heavy metals from industrial wastewater. Adsorption is considered quite attractive in terms of its efficiency of removal from dilute solutions. Many adsorbents have been used for removal of lead ions [1,2]. These adsorbents were used in raw state [3,4] or with modified surface[5,6,7]. Agricultural materials contain proteins, polysaccharides and lignin which are associated with functional groups responsible for metal ion adsorption [8]. The abundant natural occurrence and presence of large amount of surface functional groups make various agricultural wastes good alternatives to expensive synthetic adsorbents [9]. In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, banana pith, soybean and cottonseed hulls, peanut, shells, hazelnut shell, rice husk, sawdust, wool, orange peel, and compost and leaves [10]. The use of orange peel as a biosorbent material presents strong potential due to its high content of cellulose, pectin (galacturonic acid), hemicellulose and lignin. As a low cost, orange peel is an attractive and inexpensive option for the biosorption removal of dissolved metals. Orange peel employed for metal ions removal from simulated wastewater [11,12]. Some authors reported the use of orange waste as a precursor material for the preparation of an adsorbent by common chemical modifications such as alkaline, acid, ethanol and acetone treatment [13,14,15,16,17].

Thus, there is a growing demand to find relatively efficient, low cost and easily available adsorbents for the adsorption of lead, particularly if the adsorbents are the wastes [18]. The present study was carried out to show the potential of lead adsorption on a fruit material: orange peel, coming from commercial orange and which constitute a waste. The aim of this research, were to evaluate the adsorption behavior of Pb^{2+} onto microwave assisted orange peel powder. The influence of experimental conditions, contact time, pH solution, adsorbent dose, contact time, temperature and initial Pb^{2+} concentration on the adsorption behavior was investigated.

2. Materials and Methods

2.1. Preparation of the adsorbent

The experiments were carried out using the adsorbent orange peel. Orange peels were collected from the local area and washed several times with distilled water to remove dust and other impurities. Then drying, it was ground using

domestic mixer and sieved to 300 mesh size. The sample is washed with distilled water to remove colour and dried in an oven at 80^0C for 24 hours. The dried orange peel powder was carbonized on muffle furnace for 5 Hours at 500^oC. This carbonized orange peel again activated in domestic microwave (900MW) for 30 minutes. The microwave assisted carbonized orange peel (MACOP) then washed with deionised water to remove colour and other impurities. This MACOP was dried at 110^0C in vacuum oven for 24 hours, grind well and kept in air tight plastic bottles for further use.

2.2. Preparation of stock solution of Pb (II)

All reagents used are of analytical reagent grade. A Stock solution of 1000 ppm of Pb (II) ion was prepared by dissolving lead nitrate hexahydrate [Pb $(NO_3)_3.6H_2O$] in deionised water. Adsorption experiments were conducted to study the influence of adsorption parameters such as pH, initial Pb(II) ion concentration, adsorbent dose, contact time and temperature by using microwave assisted carbonized orange peel (MACOP).

2.3. Adsorption Experiment

Batch adsorption experiments of lead were carry out to determined the adsorption capacity of orange peel (MACOP) at different Pb (II) ion concentrations ranging from 20 to 140 ppm and a fixed amount 1.0 gm. of orange peel (MACOP) as bio - adsorbent in order to calculate the adsorption constant using different isotherms. 100 ml of different concentration of Pb (II) solutions ranging from 20–140 ppm were used. Orange peel (MACOP) was added to flasks and agitated at 30^0C and 180 rpm for 60 min for lead. The initial and final concentrations of the solutions were measured and determined by Atomic Absorption spectrophotometer (AAS) at the maximum adsorption wavelength and the adsorption capacities of the adsorbent were calculated. After equilibrium was attained, the metal uptake capacity for each sample was calculated according to a mass balance on the metal ion using equation (1):

$$q_e = \frac{(Co - Ce)\ V}{m} \qquad (1)$$

Where *m* is the mass of adsorbent (g), *V* is the volume of the solution (L), C_0 is the initial concentration of metal (mg L^{-1}), C_e is the equilibrium metal concentration (mg L^{-1}) and q_e is the metal quantity adsorbed at equilibrium (mg/g). Experiments were carried out at different initial pH values. The initial pH of the solution was adjusted with either HCl or NaOH. The percent removal of metals from the solution was calculated by the following equation (2) :

$$\% \ Removal = \frac{(Co - Ce)}{Co} X\ 100 \qquad (2)$$

Where C_0 (mg/L) is the initial metal ion concentration and C_e (mg/L) is the equilibrium metal ion concentration in the solution.

3. Results and Discussion

3.1. Effect of pH on Pb (II) adsorption

Figure 1. illustrated that pH obviously influenced the removal efficiency of the lead ions in the aqueous solution. The results indicated that Pb (II) removal was increased to maximum and then decreased with pH variation from 2 to 10 keeping all other parameters constant (adsorbent dose = 1 g, initial Pb (II) concentration = 100 ppm, contact time= 60 min, agitation speed = 180 rpm and T = 30°C). The maximum % removal of Pb (II) was about 82% at pH 6. The increase in metal removal with increase in pH values can be explained on the basis of a decrease in competition between proton and the metal cations for the same functional groups and by the decrease in positive charge of the adsorbent which results in a lower electrostatic repulsion between the metal cations and the surface.

3.2. Effect of Contact time on Pb (II) adsorption

Figure 2, indicated that metal ions removal was increased with an increase in contact time before equilibrium was reached. All parameters such as pH, adsorbent dose, etc. were kept constant (pH = 6, adsorbent dose = 1 g, initial Pb (II) concentration = 100 ppm, agitation speed = 180 rpm and T = 30°C). The results indicated that Pb (II) removal was increased from 43 to 82% with the contact time variation from20 to 60 minutes. At 60 minutes, the percentage removal of Pb (II) remains constant (82%), which showed that equilibrium was reached at 60 minutes itself. Thus the results illustrated that the optimum contact time for maximum removal (82%) of Pb (II) was 60 minutes. This result is important because equilibrium time is one of the important parameters for an economical wastewater treatment system.
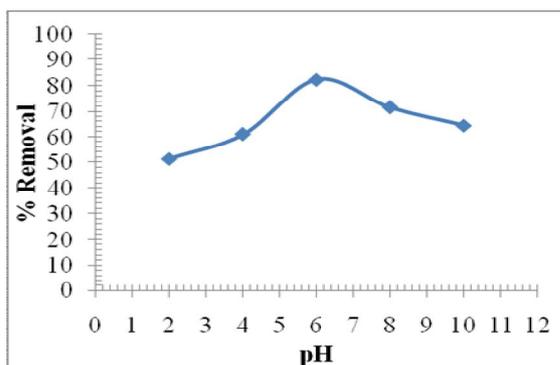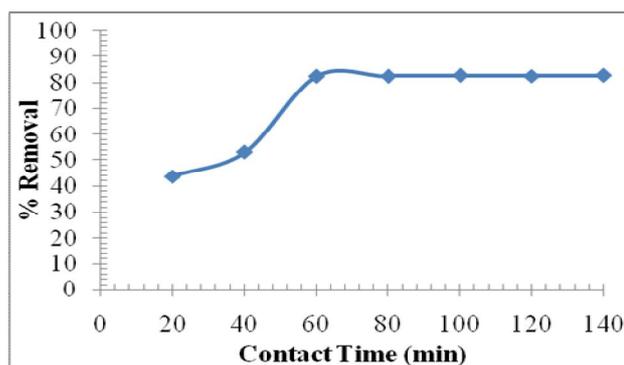
Fig 1. : Effect of pH   **Fig 2. :** Effect of contact time

3.3. Effect of adsorbent dose on Pb (II) adsorption

Adsorption efficiency of Pb (II) adsorption was studied by varying the amount of adsorbents from 0.2-2 gm keeping other parameters constant (pH = 6, initial Pb (II) concentration = 100 ppm, contact time = 60 minutes, agitation speed = 180 rpm and T = 30°C). Figure 3. shows that removal efficiency of the lead usually improved on increasing adsorbent doses. This may occur due to the fact that the higher dose of adsorbents in the solution provides the greater availability of exchangeable sites for the ions. From the figure 3, it is clear that the no further increase in adsorption after a certain amount of adsorbent was added (1 gm). The maximum % removal of Pb (II) was about 82% at the dosage of 1 gm. This result also suggest that after a certain dose of adsorbent, the equilibrium conditions reached and hence the amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent [19].

3.4. Effect of temperature on Pb (II) adsorption

The temperature dependence of the adsorption process is related with several thermodynamic parameters. The temperature showed the negative effect on adsorption of lead onto microwave assisted orange peel powder (MAOPP) as bio-adsorbent. The temperature effect on removal of lead ion using was studied within the range of 30^0C to 40^0C keeping other parameters constant (pH = 6, adsorbrnt dose = 1 g, initial Pb (II) concentration = 100 ppm, contact time = 60 minutes and agitation speed = 180 rpm). With increase in temperature from 30^0C the percent removal of l ead ions was decreased from 82% to 64%. From the figure 4, it is clear that the low temperatures are in favors of lead ion removal. This may be due to a tendency for the lead ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The result shows that adsorption mechanism related with removal of physical is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in general related with low adsorption heat. This implies that the adsorption process was exothermic in nature [19].

3.5. Effect of initial Pb (II) ion concentration on adsorption

The effect of initial lead ion concentration on the adsorption rate was studied in the rage 20 – 140 ppm at pH 6, adsorbent dose 1 g, contact time 60 minutes, agitation speed 180 rpm and temperature 30ºC. The results presented in the figure 5. It was observed that the percentage of removal decreased with increasing in initial lead ion concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of lead to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial lead ion concentration. Therefore it was evident from the results that lead adsorption was dependent on the initial metal concentration [19].
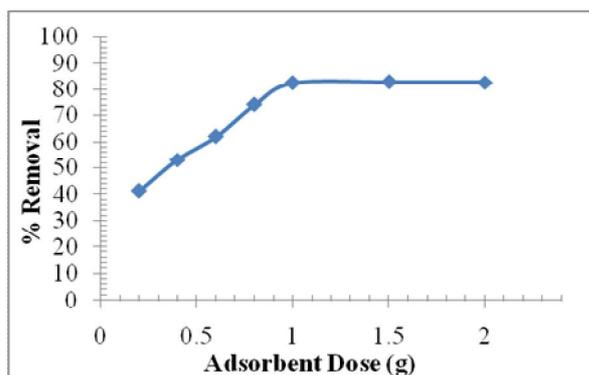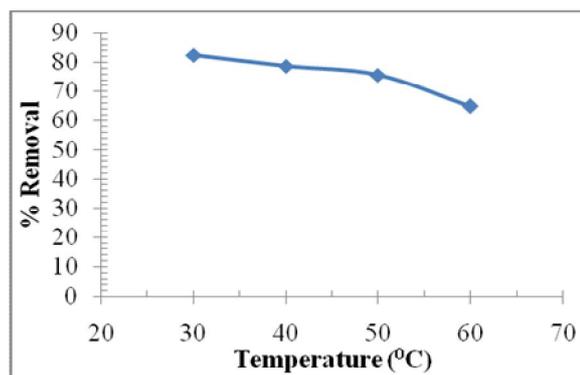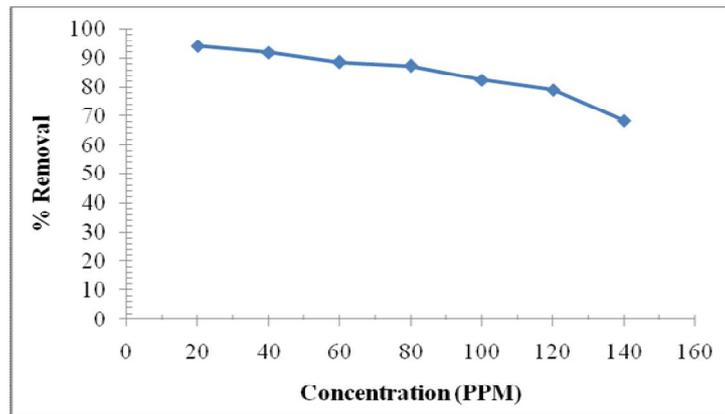

Fig. 3 : Effect of adsorbent dose   **Fig. 4 :** Effect of temperature

Fig. 5 : Effect of initial Pb (II) ion concentration.

3.6. Adsorption Isotherms

The Freundlich and Langmuir models are the most frequently used models to describe the experimental data of adsorption isotherms. Here, both models were used to investigate how Pb (II) ions interact with adsorbents, the Langmuir and Freundlich models were applied to describe the isotherm data obtained at 30^0C temperatures. The Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies. It is represented as:
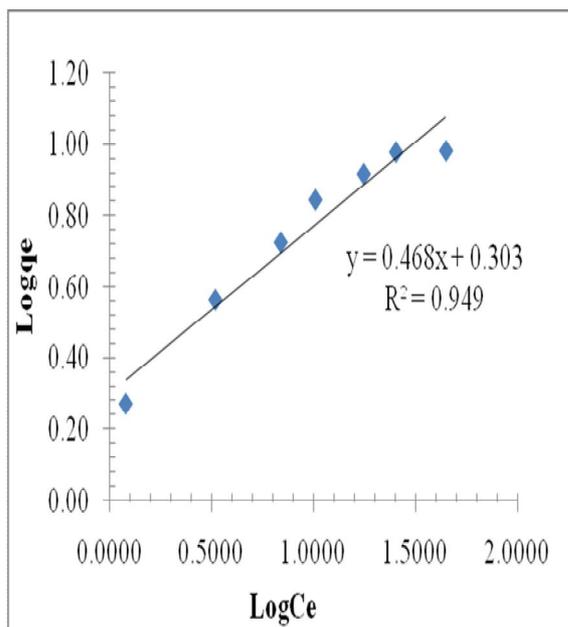
$$ln q_e = ln K_F + (1/n) \ln C_e \qquad (3)$$

Where, K_F (Lg-1) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Langmuir isotherm assumes a surface with homogeneous binding sites, equivalent sorption energies, and no interaction between adsorbed species. Its mathematical form is written as:
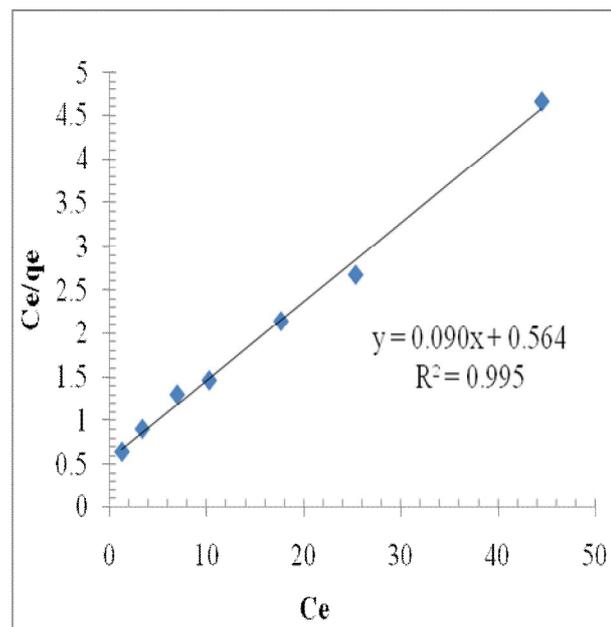
$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (4)$$

Where, q_m and K_L represent the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

Langmuir and Freundlich adsorption isotherms for from aqueous solution are presented in Figures 6 and 7 as shown below. It indicates that the experimental data fitted well to all the isotherm models. By comparing the correlation coefficients, it was observed that Langmuir isotherm gives a good model for the adsorption system, which is based on monolayer sorption on to the surface restraining finite number of identical sorption sites. The values of various constants of the two models were calculated and were represented in the Table-1.

Fig. 6 : Freundlich adsorption isotherm

Fig. 7 : Langmuir adsorption isotherm.

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Table-1. : Parameters of Freundlich and Langmuir adsorption isotherms for Pb (II) at 30^0C.

Langmuir Isotherm			Freundlich Isotherm		
q_m (mg/g)	K_L (L/g)	R^2	K_F	n	R^2
11.11	0.1595	0.995	2.009	2.136	0.949

3.7. Adsorption Kinetic Study

The kinetic study of adsorption in wastewater plays an important role because it affords important insight into the reaction pathways and into the mechanism of the reaction. Pseudo first order kinetic model and Pseudo second order kinetic model have been proposed to explain the mechanism of a solute sorption from aqueous solution onto an adsorbent.

The pseudo first-order kinetic model has been widely used to predict the metal adsorption kinetics. The metal adsorption kinetics following the pseudo first-order model [20] is

$$\frac{dq}{dt} = K_1 + (q_e - q_t) \qquad (5)$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption, q_t (mg/g) denotes the amount of adsorption at time t (min) and q_e (mg/g) is the amount of adsorption at equilibrium.

After definite integration by application of the conditions $q_t =0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (5) becomes,

$$log(q_e - q_t) = \log q_e - \left(\frac{k}{2.303}\right)(t) \qquad (6)$$

By plotting $log (q_e-q_t)$ versus t, the adsorption rate can be calculated.

The adsorption kinetic data can be further analyzed using Ho's pseudo second-order kinetics [20]. This is represented by

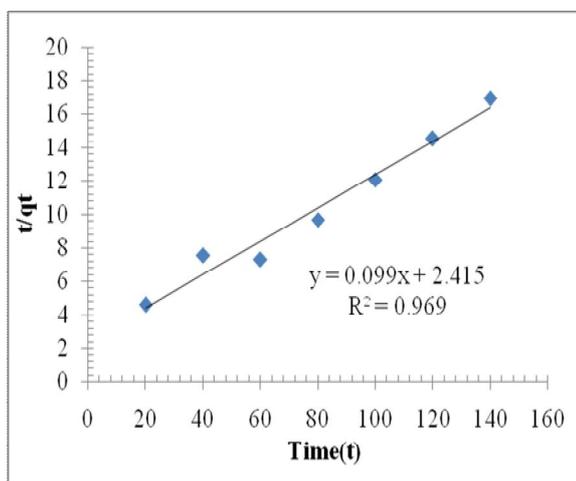$$\frac{dq}{dt} = K_2 (q_e - q_t)^2 \qquad (7)$$

Integration of Eq. (7) and application of the conditions $q_t=0$ at $t = 0$ and q_t gives,

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 \, q_e^2}\right) + \left(\frac{1}{q_e}\right) \, t \qquad (8)$$

Where k_2 (g/(mg min)) is the rate constant, k_2 and q_e can be obtained from intercept and slope.
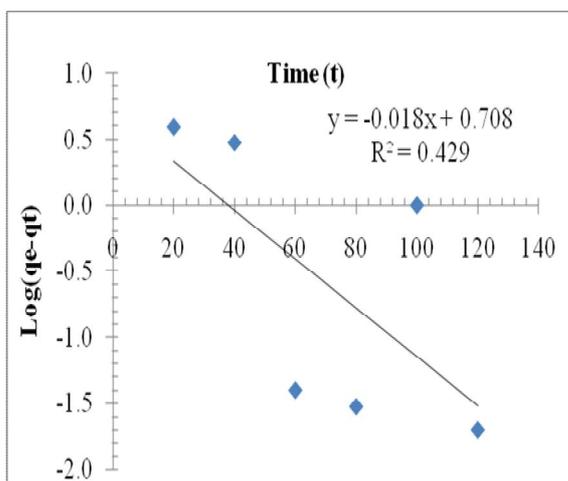
Fig. 8 : Pseudo first order model.   **Fig. 9 :** Pseudo second order model.

The kinetics of adsorption was studied for a contact time ranging 20 –140 min. The experimental data was fitted to the pseudo first order and pseudo second order kinetic model (Figure 8 and 9). The reported R^2 value indicates that the experimental results shows better fit to pseudo-second order model. Hence, the adsorption seems to be more pseudo-second order.

3.8. Thermodynamic Parameters

Thermodynamic analysis provides valuable information on the mechanism of adsorption. The thermodynamics of Pb (II) adsorption microwave assisted orange peel powder (MAOPP) were studied using the free energy change, ΔG°, according to Equation (9):

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$$\Delta G = -RT \log K \qquad (9)$$

The plot of logK vs. 1/T (Figure 10) gives a straight line and the values of $\Delta S°$ and $\Delta H°$ can be obtained from its intercept and slope, respectively. The calculated values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ are presented in Table 2. The negative value of ΔG^0 at all temperatures indicates that the lead adsorption reaction was spontaneous in nature. As the ΔG^0 ranges from 1.912 to 4.275 kJ/mol, the adsorption process is predominantly a physical adsorption process.
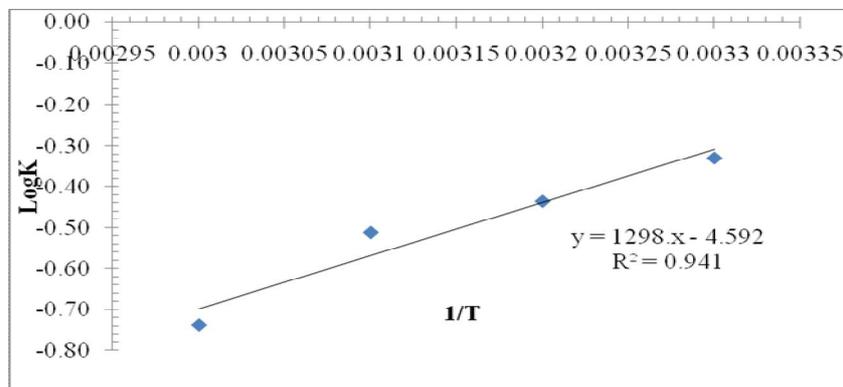
Fig. 10 : The plot of logK vs. 1/T

TABLE-2 :- Thermodynamic parameters of adsorption.

T(K)	ΔG (kJ/mole)	ΔH (kJ/mole)	ΔS (kJ mol^{-1} K^1)
303	1.912		
313	2.523	24.852	0.0879
323	2.965		
333	4.275		

4. Conclusion

The present investigation shows that the microwave assisted carbonized orange peel (((MACOP) can be employed as a potentially low cost adsorbent for the removal of Pb (II) ions from wastewaters. The Pb (II) adsorption is found to be greatly dependent on the initial pH of the solution, its concentration, contact time, temperature and adsorbent dose. The maximum adsorption of Pb (II) was found at pH values 6. The kinetic experiments show that the adsorption was rapid and the adsorption equilibrium was achieved in 60 min of contact time. The equilibrium data are well described by the Langmuir isotherm model (R^2 value 0.995). Kinetic studies of adsorption revealed that the adsorption process followed a pseudo second order kinetic model. Thermodynamic parameter of adsorption studies revealed that the adsorption of Pb (II) using microwave assisted carbonized orange peel is a physical adsorption phenomenon. These results show that adsorbents which have a very low economical value may be used effectively for removal of Pb (II) ions from aqueous systems for environmental protection purpose.

5. Acknowledgement

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