RESEARCH ARTICLE

ADSORPTION OF NICKEL (II) AND LEAD (II) IONS FROM A STOCK SOLUTION USING MORINDA CITRIFOLIA CARBON AS A LOW-COST ADSORBENT

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ABSTRACT

In present study the adsorption of metal ions on activated carbon of morinda citrifolia has been studied using Atomic adsorption spectroscopy for metal estimation. The influence of various parameters like heavy metal ion concentration, adsorbent dose, pH of the adsrobate and contact time were studied. Langmuir and freundlich isotherms and kinetic modeling were employed to describe adsorption equilibrium. The values showed that morinda citrifolia carbon has a better sorptive potential and could be used as low cost adsorbents for the removal of lead(II) nickel(II) from aqeous solution.

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INTRODUCTION

Increasing pollution of municipal and industrial sewages by toxic compounds due to industry development and growth is a concerning issue. Heavy metal pollution is a environmental problem of Global concern (3) Nickel, Lead are non-biodegradable present in the waste water released from industrial process such as galvanization, smelting, mining, dyeing operation, battery manufacturing, metal finishing and textile industry. These heavy metals have been recoganized as harzards. Therefore it is necessary to develop effective and inexpensive methods to remove toxic metals from waste water. The aim os this study was to investigate the removal efficiency of heavy metals such as Nickel (II), Lead (II) with activated carbon prepared from Morinda Citrifolia bark as low cost adsorbent. in the region. The effective parameters on adsorption process such as contact time, pH, initial concentration, adsorbent dosage of metal ions were studied the Langmuir and Freundlich adsorption isotherm,kinetic studies were studied.

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MATERIALS AND METHODS

Adsorbent preparation

Preparation of activated Carbon (AMC) was prepared by treating air-dried barks of morinda citrifolia, with concentrated sulphuric acid a weight ratio of 1:1. The resulting black product was kept in a furnace, maintained at 500°C 12 h followed by washing with water until free from excess acid and dried at 150 °C±5 °C. The carbon product was ground and was used as adsorbents for all the experiments. The adsorbent made into 0.75μm—150 μm size and it was allowed into the mechanical sieving machine manufactured by Jayanth scientific industries, Mumbai.

Adsorbate preparation

1000 mg/L of nickel(II), lead(II) solutions was prepared by dissolving 1.5986g of lead sulphate and 6.809 g of nickel ammonium sulphate in double-distilled water and making up to 1000 ml. The stock solution was diluted to obtain required standard solutions. The concentrations of metal ions in the nickel (II), lead (II) solutions after equilibrium were determined by Solar A2 Solaram Atomic Absorption spectrophotometer. The pH of the solution adjusted by 1M HCl

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and the pH was measured with a systronics digital pH meter using a combined glass electrode. The shaking was carried out in a mechanical shaker with rpm of 225, manufactured by Macro scientific works, Jawaharlal Nagar, Delhi-7.

Adsorption experiment

Batch mode experiments were conducted using 250mL Erlenmeyer flasks by contacting 50mL of the aqueous Ni (II), pb(II) solutions of different initial concentrations. The initial pH of the solution was adjusted before starting each experiment. The experiments were performed in a mechanical shaker for a period of 90 minutes at room temperature. The remaining concentration of Ni (II), pb(II) ions in each sample after adsorption at different time intervals was determined by atomic absorption spectroscopy after filtering the adsorbent with Whatmann filter paper No.40 to make it adsorbent free. The Ni(II),pb(II) concentration retained in the adsorbent phase was calculated.

$$\text{Metal removal (\%)} = 100(C_i - C_e)/ C_i \qquad \text{--------(1)}$$

Where qe equilibrium Ni (II), pb(II) concentration, C_i and C_e are the initial and equilibrium concentrations (mg/L) of Ni (II),pb(II) solution respectively. V is the volume (L), and W is the mass (g) of the adsorbent.

RESULTS AND DISCUSSION

Effect of initial concentration

The nickel (II), lead(II) removal on AMC was studied as a function of initial concentrations (2,4,6,8,10,15,25mg/L). The effect of initial metal ion concentration from aqueous solution shown in Figure 1. At the same time, the percent removal of (Fig. 1) sharply decrease with the increasing of the initial concentration.
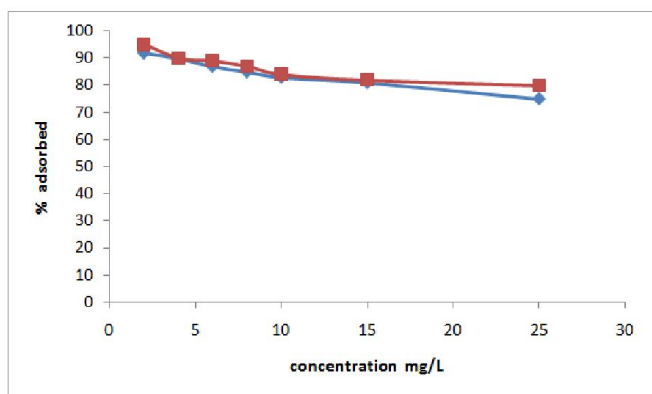

Fig. 1. Effect of initial concentration

Effect of pH

This opposite trend is determined by the fact that at higher concentrations, the diffusion of metal ions to the un-reacted functional groups is inhibited. Hence an optimum concentration of 2 mg/L was chosen for subsequent studies. The initial pH of the solution was adjusted before starting each experiment. The experiments were performed in a mechanical shaker for a period of 90 minutes at room temperature. The remaining concentration of (II) ions in each sample after adsorption at different time intervals was determined by atomic

absorption spectroscopy after filtering the adsorbent with Whatmann filter paper No.40 to make it adsorbent free.
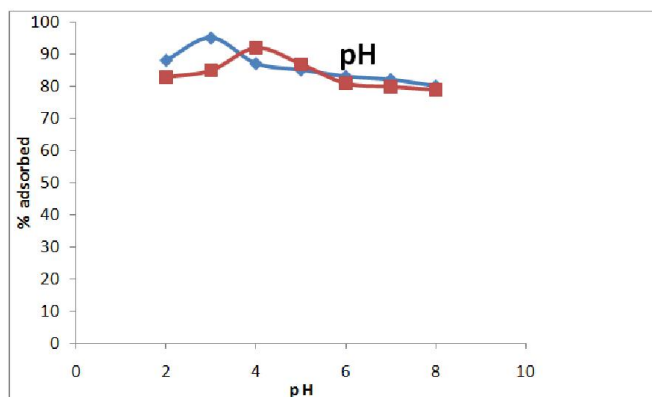

Fig. 2. pH

The metals concentration retained in the adsorbent phase was calculated as equation 2.

$$qe = (C_i - C_e) V / W \qquad \text{---------(2)}$$

Where qe metals concentration, C_i and C_e are the initial and equilibrium concentrations (mg/L) of nickel(II), lead(II) (Venkatraman et al., 2012) solution respectively. V is the volume (L), and W is the mass (g) of the adsorbent.

Effect of contact time

Contact time profile for the adsorption of nickel, lead for a solution of 2 mg/L is shown in the data obtained from the adsorption of metal ions on the morinda citriflia carbon showed that a contact time of 90 minutes for nickel, for lead 80 minutes is needed to achieve equilibrium. The adsorption decreases significantly with further increase in contact time (Figure 3).
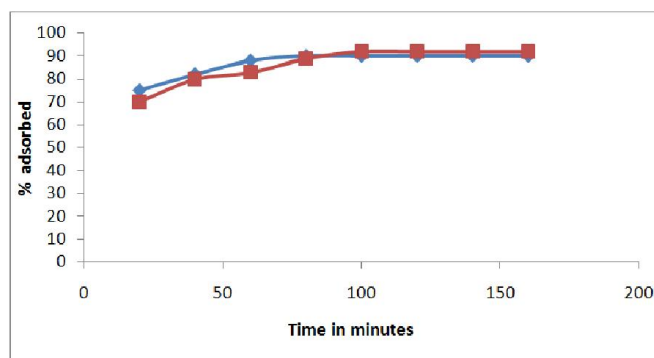

Fig.3. Effect of time on metal ions

Effect of adsorbent dosage

Effect of adsorbant dosage (Amala Fatima Rani et al., 2012) on adsorption of nickel(II), lead(II) is studied by changing the adsorbent dosage from 0.1g` to 1g and there is no change in other parameters like initial concentration. The contact time was 90 minutes for nickel, 80 minutes for lead as stated earlier. The graph shows an increase in the adsorption percentage as dosage of bio sorbent increases to certain level (Figure 4). This is because of the availability of more binding sites in the

surface of the ad sorbent for complexation of metalions. The beginning the progressive increase in adsorption and consequently the attainment of equilibrium adsorption may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of adsorbent.

Equilibrium Study

Sorption isotherms usually describe the equilibrium relation between sorbent and sorbate, that is the equilibrium relationship between the quantity of metal sorbed and that remaining in aqueous solution as a fixed temperature. By plotting solid mass concentration against liquid phase concentration, it is possible to predict the equilibrium isotherm. The isotherm thus yields certain constants whose values express the surface properties and affinity of the sorbent. Adsorbent data are usually described by adsorbent isotherms, like Langmuir and Freundlich isotherms.
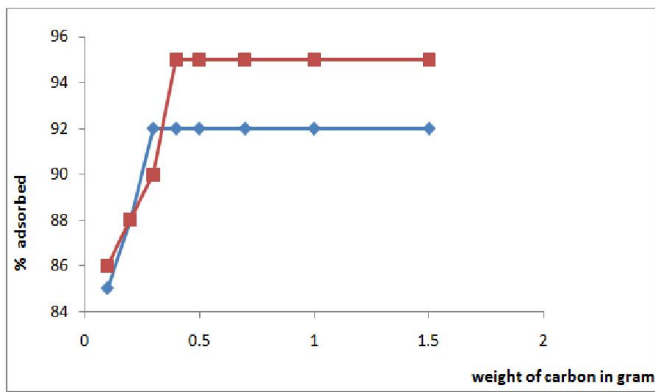

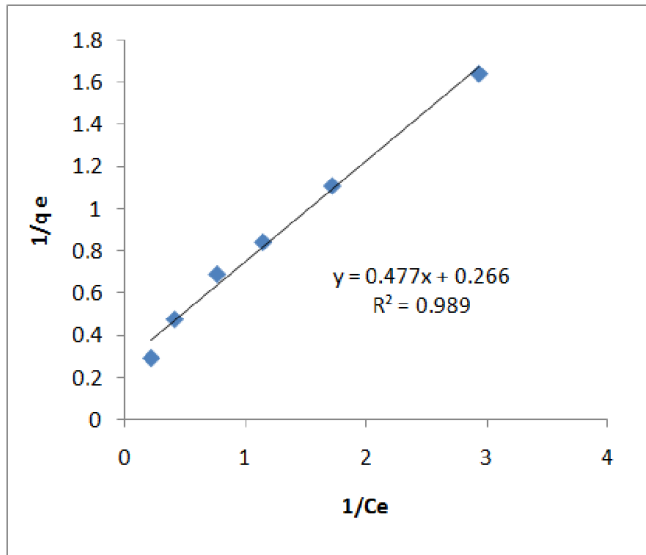**Fig.4.Effect of adsorbent dosage on metal ions**

Fig.5. Langmuir isotherm on metal ions (Nickel)

Figure. 5 shows the logarithemic plot of Freundlich expression eqn 5&6 for the amount of Ni(II) &pb(II) adsorbed unit mass of the adsorbate (q_e) and the concentration (Ce) at equilibrium. The values of K_F and n are calculated from the slope and intercept of the plot figure 7&8. Table 1 shows the Freundlich Langmuir constants and linear correlation coefficient for the adsorption of 2mg/L of Ni(II) &pb(II) solution onto morinda citrifolia carbon.
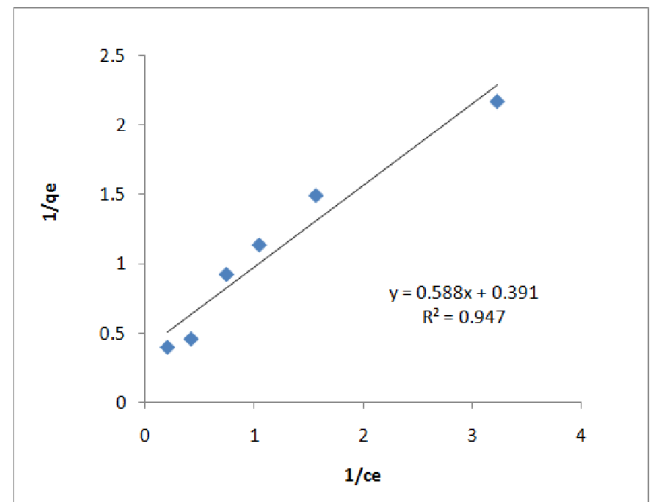

Fig.6. Langmuir isotherm of metal ions (lead)

The Langmuir Model

The Langmuir model is based on the assumption that the maximum adsorption occurs when the saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the plane. The Langmuir isotherm is given by

$$q_e = q_m K_L C_e / (1 + K_L C_e) \qquad \text{-------------(3)}$$

The constants in the Langmuir isotherms can be determined by plotting (1/qe) versus (1/ce) and writing the above equation as;

$$1/q_e = 1/q_m + (1/q_m K_L)(1/C_e) \qquad \text{----------------(4)}$$

Where q_m and K_L are the Langmuir constants, represent the maximum adsorption capacity or the solid phase loading and the energy constant related to the heat of adsorption, respectively. It can be seen from Figure 4 that the Langmuir eqation fitted well $R^2 = 0.991$. The values of q_m and K_L were determined from Figure 4.

Freundlich isotherm

The Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent

$$\ln qe = K_F C_e^{1/n} \qquad \text{------------(5)}$$

The equilibrium can be linearized by taking logarithms to find the parameters K_F and n

$$\ln q_e = \ln K_F + (1/n) \ln C_e \qquad \text{------------(6)}$$

Adsorption kinetics

The kinetics study for the adsorption of Ni(II) & pb(II) was completed in equlibrium minutes for the concentrations 2mg/L, of morinda citrifolia activated carbon at room temperature.
The experimental results for the adsorption of Ni(II) & pb(II) ions showed rapid initial adsorption rate followed by a slower rate. (De, 4th edition) Initially, the adsorption sites are open and the metal ions interact easily with the sites and hence a higher rate of adsorption is observed. Further, the driving force for adsorption (the concentration difference between the bulk

solution and the solid-liquid interface) is higher initially and this leads to a higher adsorption rate. However, after the initial period, slow adsorption may be due to slower diffusion of solute into the interior of the adsorbent (Jiang *et al.*, 2010). Several adsorption kinetics models have been developed to understand the adsorption kinetics and rate limiting step. Two kinetic models were considered to investigate the mechanism of metal adsorption, Lagergren proposed a pseudo-first order kinetic model, the integral form of the model is:

$$dq/dt = k_1(qe - qt) \qquad \text{------------------- (7)}$$

$$\log (qe - qt) = \log \ qe \ -(K_{1\ ads} / 2.303) \ t \qquad \text{-------------(8)}$$

where qe is the amount of nickel sorbed (mg/g) at time t (min), qe is the amount of nickel sorbed at equilibrium (mg/g), K_1 is the equilibrium rate constant of pseudo-first order adsorption. This model was successfully applied to describe the kinetics of many adsorption systems. The adsorption kinetics may also be described by a pseudo-second order reaction. The linearized-integral form the model is:

$$dq/dt = k_2(qe - qt)^{2-} \qquad \text{-------------------- (9)}$$

$$\bullet t/qt = t/qe + 1/ \ k_2\,qe^{\ 2} \qquad \text{------------------(10)}$$

where K2 is the pseudo-second order rate constant of adsorption of the above two models can be examined by each linear plot of ln(qe-qt) vs. t, and (t/qt) vs t, respectively. To quantify the applicability of each model, the correlation coefficient, R^2 Figure 9&10, was calculated from these plots.

The linearity of these plots indicates the applicability of the two models. However, the correlation coefficient, R^2, showed that the pseudo-second order model, fits better the experimental data than the pseudo-first order model, the kinetic parameters calculated are shown in Table 2. It has been found that, the equilibrium sorption capacities determined using pseudo-second order model were in agreement with the experimentally determined equilibrium sorption capacities. Also, the rate constant decreased with the solution concentration increasing. In general, the adsorption reaction is known to proceed through the following three steps: (1) transfer of adsorbate from bulk solution to adsorbent surface, which is usually mentioned as diffusion, (2) migration of adsorbate into pores and (3) interaction of adsorbate with available sites on the interior surface of pores.

RESULTS

The maximum removal efficiency of heavy metals (nickel and lead) by activated carbon adsorbent prepared from morinda citrifolia was obtained. The optimum amount of adsorbent was 0.3 g, and the optimum contact times were 80 minutess for nickel and 120 minutes optimum contact time, 0.4g optimumamount of adsorbent for lead ion, respectively. In these optimum conditions the removal efficiencies were optimum conditions were 92% and 95%, respectively. The results obtained showed the highest correlation with Langmuir & freundlich isotherm model and the kinetic studies showed that the data well fitted in pseudo second order than pseudo first order.

Table 1. Sorption Isotherm Constants

Langmuir constants			Freundlich constants			
q_m mg/g	K_L	R^2	K_F	n	R^2	METALS
3.7593	0.5577	0.9892	1.2019	1.4925	0.996	Ni
2.5575	0.649	0.947	0.9618	1.5408	0.979	Pb

Table 2. Kinetic modeling

K_1 ads.	qe mg/g	R^2	K_2 ads.	qe mg/g	R^2	metals
0.02763	0.1073	0.969	0.5454	0.3087	0.998	Ni
0.0368	0.1592	0.877	0.395	0.2487	0.996	Pb

y = 0.674x + 0.211
R² = 0.996
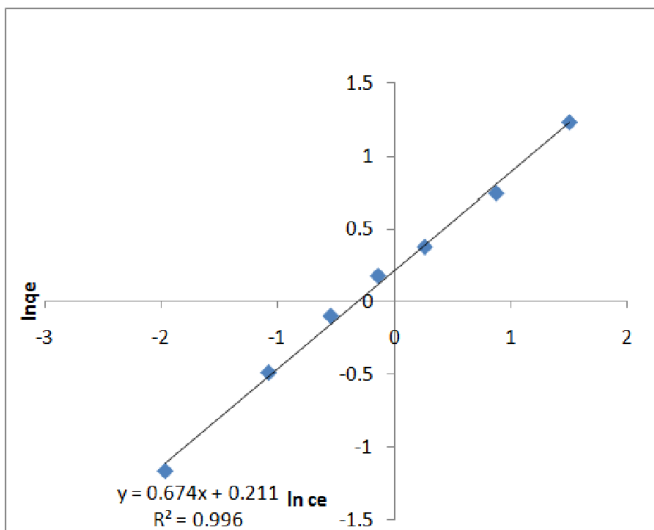
Fig.7. Freundlich isotherm of metal ions (nickel)
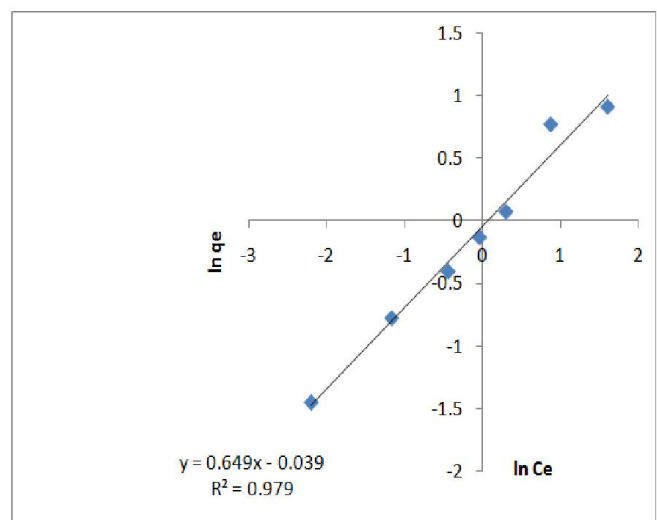

y = 0.649x - 0.039
R² = 0.979

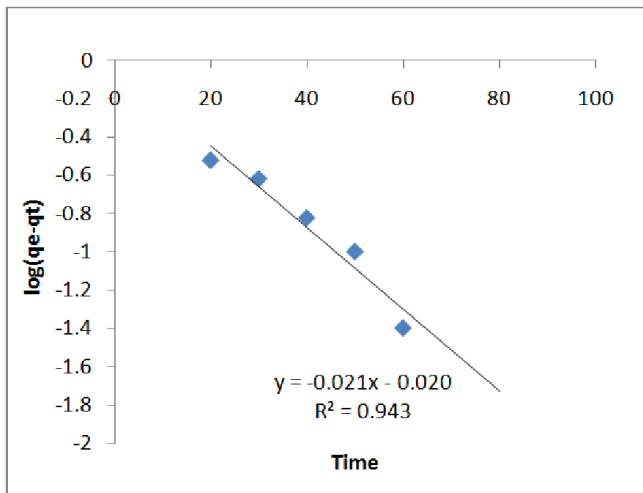**Fig.8. Freundlich isotherm ofmetal ions (lead)**

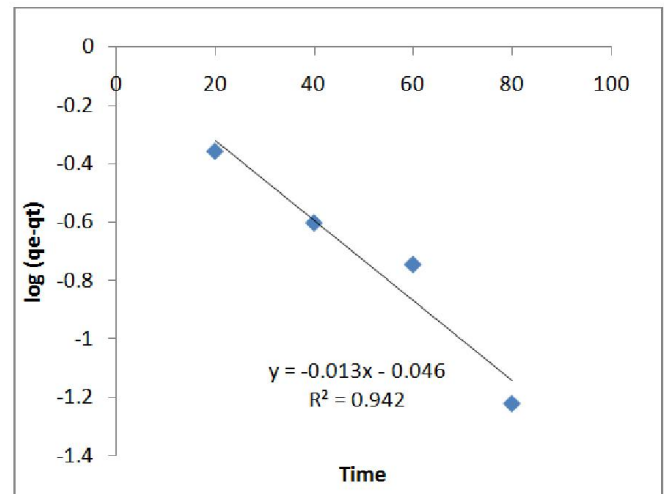**Fig.9. Pseudo first order of Ni**

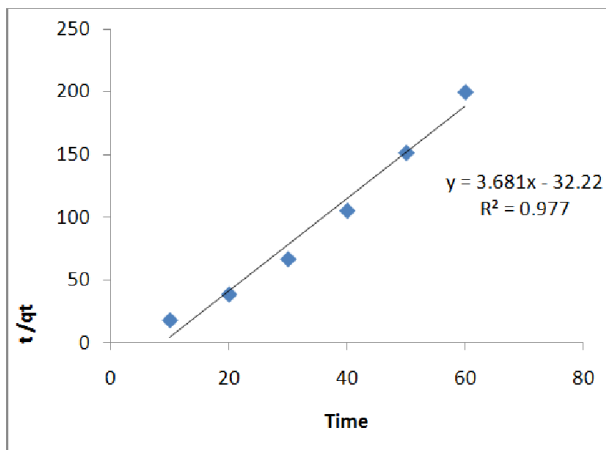**Fig.10. Pseudo first order of Pb**

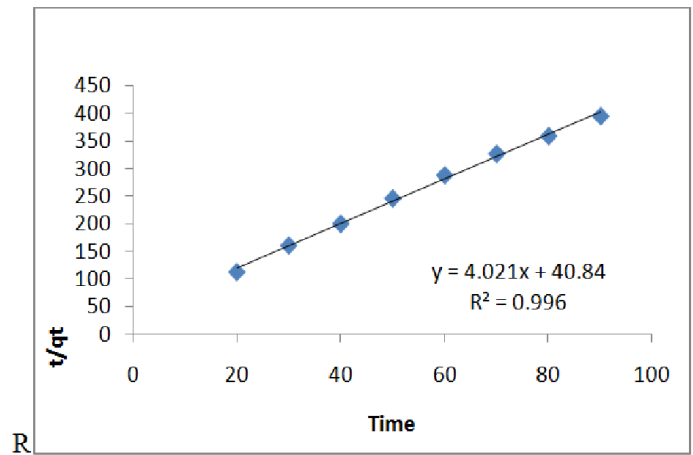**Fig.11. Pseudo second order of Ni**

Fig.12. Pseudo second order of Pb

Conclusion

Based on the results obtained, the activated carbon produced from morinda citrifolia activated carbon has a good capability in removal of the metal ions from the aqueous solutions. Considering the availability of morinda citrifolia bark and, its cost-effectiveness, and high uptake capacity, it can be applied as a proper adsorbent to remove the heavy metals from industrial waste water.

Acknowledgements

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