

**ADSORPTION OF LEAD FROM AQUEOUS SOLUTION BY USING
LOW COST ADSORBENT PREPARED FROM WOOD APPLE SHELL
ACTIVATED CARBON (WASAC)**

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ABSTRACT

In the present study, Wood Apple Shell Activated Carbon (WASAC) was used to remove Pb(II) from aqueous solution, using batch experiment. Various adsorption parameters such as pH, initial

concentration of Pb(II), adsorbent dose, contact time, have been studied. The experimental data fitted well to Langmuir isotherm. The kinetic process of Pb(II) adsorption on WASAC was found to fit the pseudo- second order model. The result shows that WASAC is a good low cost adsorbent as 81% removal of Pb(II) is achieved in the present study.

KEYWORDS: Wood Apple Shell Activated Carbon (WASAC), adsorption isotherm, low-cost adsorbent, adsorption parameters.

INTRODUCTION

Heavy metal discharge from various industries into water bodies is a big environmental problem now days. These discharges generally contain heavy metals like Cr, Ni, Cu, Cd, Pb etc. which has a tendency to accumulate into water bodies and make them toxic. Pb is one of the most toxic heavy metal released by various electroplating, brass and steel industries, petrochemical industries, mining operations etc.^[1-3] Lead intoxication can affect brain functions and activity though subtly, like influencing intelligence, attention span, language, and memory. Insomnia and nightmares are often experienced. Hyperactivity and even retardation and senility may result. It also reduces immune and kidney function and increase

risk of infections, and may be another factor in increasing blood pressure. As many industries in developing countries are situated in an unorganized manner and are continuously discharging their effluent directly into rivers without any pre treatment process and are severely polluting the rivers and lakes. There is number of method like chemical coagulation, ion exchange, evaporation, sedimentation etc.^[4-7] is available for the removal of heavy metal but these technologies are very costly. Adsorption is one of the highly effective methods for the removal of heavy metal because of its cost effectiveness and high recovering capacities.^[8,20]

In the present study we use Wood apple shell to prepare activated carbon which can have good adsorption capacity. The activated carbon developed from wood apple shell was economical and have good quality, so it could be used for further application.

MATERIAL AND METHODS

Preparation of Wood Apple Shell Activated Carbon (WASAC)

Sample of wood apple (*Limonia acidissima*) was collected from local market. Wood apple shells were washed thoroughly with distilled water and kept for sun dry. After drying, the shells were crushed in small pieces and again washed with deionized water and dried in an oven at 110⁰ C for 24 hrs. The crushed pieces were soaked in concentrated H₂SO₄ for 24 hrs. This material was then washed with deionized water and was kept for activation in muffle furnace at 300⁰ C for 1 hr. The excess acid was washed off with distilled water till neutral pH was obtained. The dried activated carbon was then sieved to prepare fine powder of 200 μm particle size and used this wood apple shell activated carbon (WASAC) during the study.

Preparation of Adsorbate solution

In this study, the stock solution of Pb(II) was prepared by dissolving a known quantity of lead nitrate in deionized water. Stock solution was further diluted to obtain the required concentrations of Pb(II) solutions. 1.0 N NaOH and 1.0 N HCl were used for pH value adjustments.

Characterization of adsorbent

The surface functional groups and structures were studied by Fourier transform infrared spectroscopy (FTIR) in the WASAC before and after Pb(II) adsorption (Figure 1 & Figure 2). The FTIR spectra of WASAC were recorded between 400 & 4000 cm⁻¹. The FTIR spectra showed characteristics cellulose peak in the finger print region 1000-1200 cm⁻¹. The band

1159 cm^{-1} and 1056 cm^{-1} in WASAC related to COC group bands in cellulose and the band near 1318 cm^{-1} related to CH_2 wagging vibration in cellulose. The band near 3332 cm^{-1} represented the OH vibration. From FTIR studies, the structure appeared to be the probable structure of phosphorylated cellulose. The band near 3700 cm^{-1} in WASAC seen to be split into less intense peaks due to the change in intra molecular hydrogen bonding interactions. The band appearing at 1012 cm^{-1} describing the P-O stretching (Figure 2).^[21]

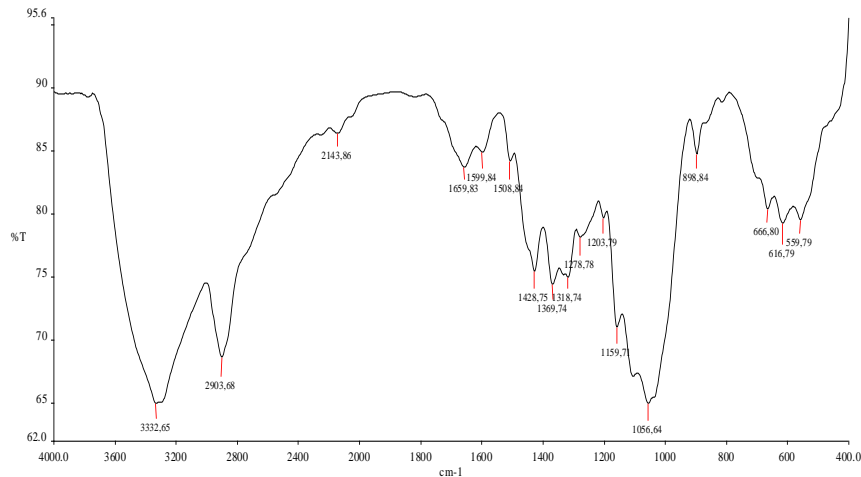


Fig. 1: FTIR spectra of WASAC before Pb(II) adsorption.

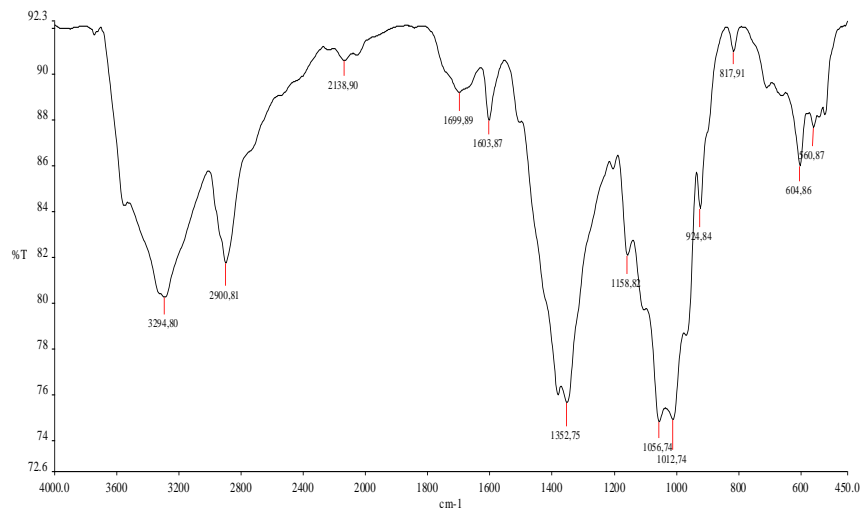


Fig. 2: FTIR spectra of WASAC after Pb(II) adsorption.

Batch adsorption experiment

Batch sorption experiments were conducted by using 50 mL aliquots of pH adjusted test solutions by varying concentrations of Pb(II) from 100 mg/L to 200 mg/L, at constant adsorbent dose 500 mg/L. While adsorbent dosage was varied from 100 mg/L to 500 mg/L at

constant concentration of Pb(II) of 100 mg/L. The effects of time, agitating speed and pH were studied with Pb(II) concentration of 100 mg/L and an adsorbent dosage of 500 mg/L. Adsorption isotherm study was done with 100 mg/L Pb(II) at 25⁰C at pH 3 and time of contact was maintained at 120 min. The agitation was done at 140 rpm in the Erlenmeyer flasks on an orbital shaker. The metal ion solution was maintained acidic throughout the study with pH 3, of each solution was adjusted with dilute HCl or NaOH. The batch adsorption experiments were carried out at room temperature at different contact times (30 to 150 min), initial concentration of Pb(II) (100 to 200 mg/L), WASAC dose (200 to 500mg /50 mL) and pH 2 to 9. The Pb(II) percent removal (%) was calculated as follows:

$$\% \text{ Removal of Pb} = [(C_i - C_e) / C_i] \times 100 \text{ ----- (1)}$$

The adsorption capacity per unit mass of the WASAC was calculated according to the following expression:

$$q_e = [(C_i - C_e) / m] \times V \text{-----(2)}$$

Where C_i and C_e are the initial and final Pb(II) concentrations (mg/L), respectively, q_e is the amount of Pb(II) adsorbed onto WASAC (mg/g), V is the total volume of solution (L), and m is the WASAC dosage (g).

RESULT AND DISCUSSION

Effect of contact time

The contact time has an important role on the adsorption of Pb(II). The amount of adsorption of Pb(II) was measured at different time intervals. At the equilibrium time of 120 min, the Pb(II) adsorption was investigated to be 81% with initial concentration of Pb(II), 100 mg/L and other conditions like temperature, agitation speed etc. were kept constant. It was observed that rate of adsorption was continuously increases up to 120 min. and the adsorption of Pb(II) was found to be 81% which remains constant thereafter (Figure 3).

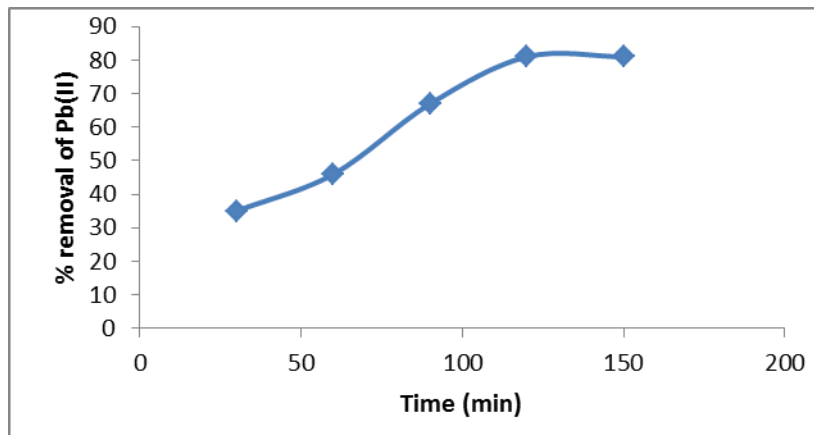


Fig. 3: Effect of time on removal % of Pb(II) on adsorption of WASAC (Pb(II) = 100 mg/L, T= 25⁰C, WASAC =500 mg, pH=3).

Effect of pH

The removal efficiency of Pb(II) on WASAC at different pH values with an initial concentration of 100 mg/L is shown in Figure 4. To each flask containing 50 mL of Pb(II) solution, 500 mg of adsorbent was added and agitated for 120 min at pH varying from 2 to 9. After agitation the solution was filtered through Whatmann filter paper no.1 and lead removal efficiency was found 81% in the pH range 2-3. Maximum adsorption of Pb(II) was observed at the acidic pH. This is because at lower pH there is increase in H⁺ ions on adsorbent surface.^[22]

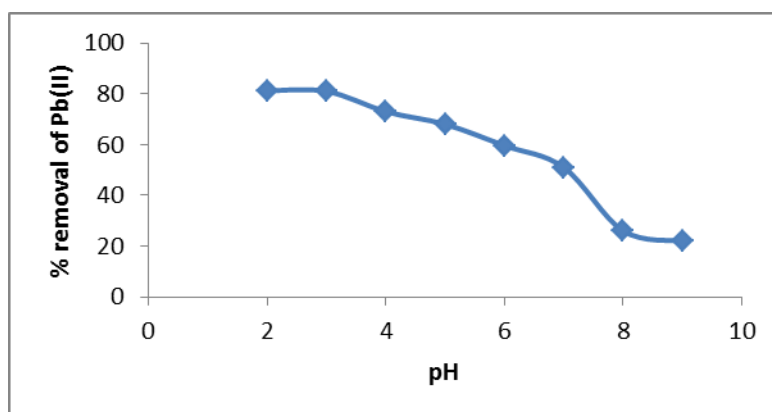


Fig. 4: Effect of pH on % removal of Pb(II) on adsorption of WASAC (Pb(II) = 100 mg/L, T= 25⁰C, WASAC =500 mg, Time = 120 min.).

Effect of initial concentration of Pb(II)

The percentage removal of Pb(II) was 81% for 100mg/L as shown in Figure 5. The pH of the system was adjusted to 3, and the agitation was done at 140 rpm for 120 min. The percentage removal of Pb(II) decreases with an increase in initial Pb(II) concentration. It may be due to

an increase in the number of Pb(II) ions for the fixed amount of WASAC. A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the metal ion between the aqueous and solid phases, thus increases the uptake.^[22]

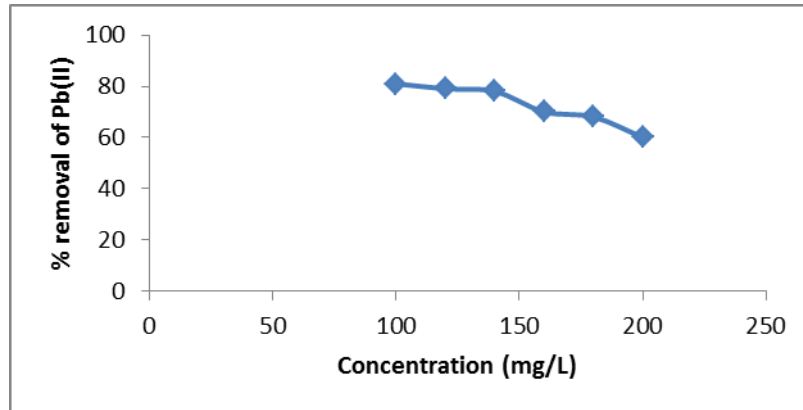


Fig. 3: Effect of initial concentration on removal % of Pb(II) on adsorption of WASAC (pH = 3, T= 25⁰C, WASAC =500 mg, Time = 120 min.).

Effect of adsorbent dosage

The experiments were carried out under the conditions described earlier and varying adsorbent dosage from 200 mg/L to 500 mg/L. The effect of adsorbent dose on the adsorption of lead by WASAC is presented in Figure 6. The Pb removal efficiency increases with increase in adsorbent dose, since contact surface of adsorbent particles increased. Maximum adsorption was observed at 500mg/L i.e. 81%. It can be observed that removal efficiency of the adsorbents generally increased with increasing the quantity. It is due to the availability of exchangeable sites for the adsorbate.^[23]

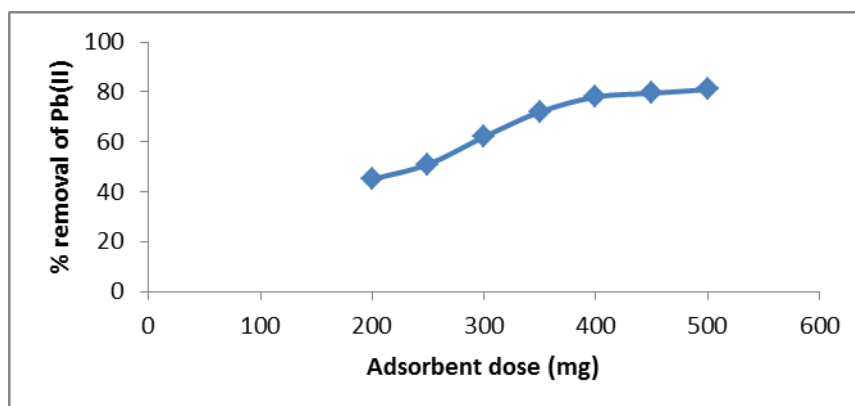


Fig. 6: Effect of adsorbent dose on removal % of Pb(II) on adsorption of WASAC (pH = 3, T= 25⁰C, Pb(II) = 100 mg/L = 100 mg/L, Time = 120 min.)

Langmuir isotherm

According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at the site. The Langmuir model is given by following Eq (3),

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

Where, C_e is the equilibrium concentration mg/L, q_e is the amount of Pb(II) adsorbed at equilibrium (mg/g) and q_m is q_e for a complete monolayer (mg/g); K_L is sorption equilibrium constant (L/mg). A plot of C_e/q_e versus C_e (Figure 7) should indicate a straight line of slope $1/q_m$ and an intercept of $1/K_L q_m$.^[24-25] The Langmuir parameters can be used to predict the affinity between the adsorbate and adsorbent using the dimensionless separation factor, R_L ,^[26] Eq. (4)

$$R_L = 1 / (1 + K_L C_e) \quad \text{-----} \quad (4)$$

The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$.

The adsorption of Pb(II) on WASAC follows the Langmuir isotherm model for metal adsorption. The dimensionless parameter R_L values lies between 0.0801 to 0.4365 is consistent with the requirement for favorable adsorption. The high value of correlation coefficient R^2 indicates a good agreement between the parameters and confirms the monolayer adsorption of Pb(II) onto the adsorbent surface.

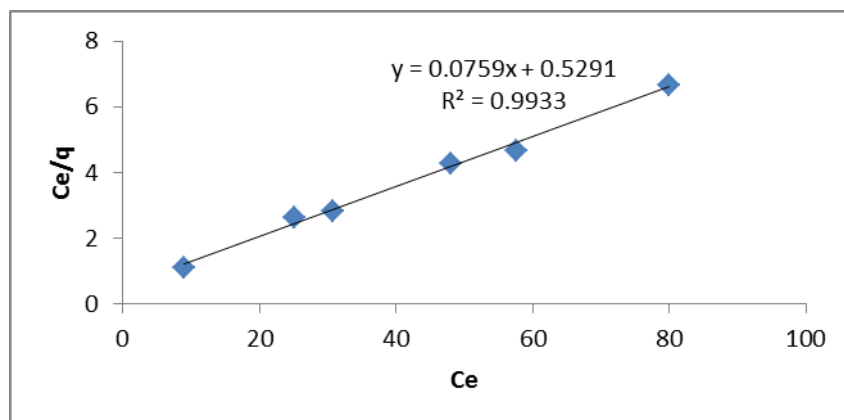


Fig. 7: Langmuir adsorption isotherm for Pb(II) adsorption on WASAC (pH = 3, T= 25°C, WASAC = 500mg, Time = 120 min.).

Freundlich isotherm

Freundlich isotherm model was also used to explain the observed phenomenon.^[27] The Freundlich isotherm is represented by Eq. (3)

$$\log q_e = \log K_f + 1/n \log C_e \text{ ----- (5)}$$

Where, C_e is the equilibrium concentration (mg/L), K_f and n are constant incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. A plot of $\log q_e$ vs $\log C_e$ (Figure 8) gives a linear trace with a slope of $1/n$ and intercept of $\log K_f$. $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favourable ($0 < 1/n < 1$) and unfavourable ($1/n > 1$).^[26] Therefore WASAC which has $1/n$ value of 0.1968 implies effective adsorption. The value of the correlation coefficient, R^2 , obtained in this case indicates that the Freundlich model gave a poorer fit to the experimental data than the Langmuir isotherm model.

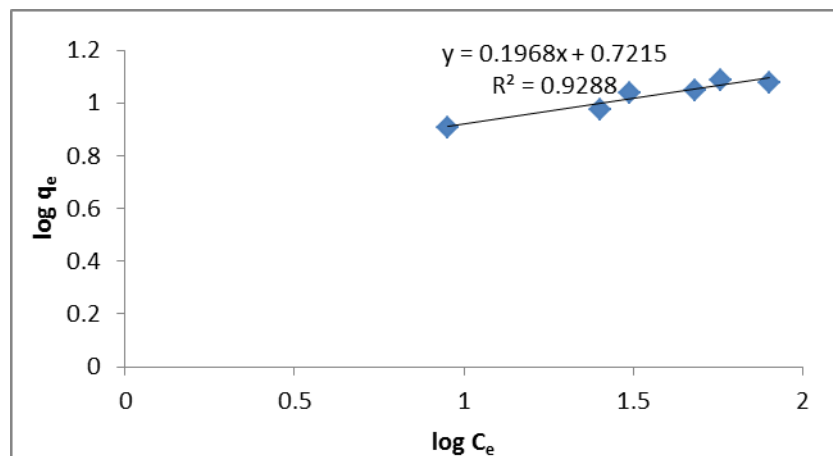


Fig. 8: Freundlich adsorption isotherm for Pb adsorption on WASAC (pH = 3, T= 25⁰C, WASAC = 500mg, Time = 120 min.).

Adsorption Kinetics

Kinetics of adsorption is one of the most important characteristic for the adsorption efficiency. Removal of heavy metal by adsorption involves number of steps. In order to investigate the mechanism of process and potential rate-controlling steps, the experimental kinetic data for the uptake of Pb(II) at different initial concentrations, which is modeled by the pseudo first order by Lagergren and the pseudo-second order by Ho and McKay [28], are given in Equations 6 and 7, respectively. The pseudo-first-order model was used to check the adsorption data of Pb(II) on WASAC, but the correlation coefficient was not high. However, the pseudo-second-order kinetic model was successfully applied with.

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

$$t/q_t = 1/k_2 \cdot q_e^2 + 1/q_e \quad \text{-----} \quad (7)$$

Very high correlation coefficient for explaining the kinetic data of the adsorption processes.^[28] The adsorption of Pb(II) on WASAC could be a pseudo-second order process rather than a first order. By comparing the figures of the pseudo-first order (Figure 9) and the pseudo-second order (Figure 10) models, it is obvious that the pseudo-second-order model fits the experimental data better than the pseudo first order for the entire adsorption period. By comparing the coefficient of determination R^2 in Figure 9 and Figure 10, it is observed that the pseudo-second order model fits the experimental data with higher R^2 values (0.9156 to 0.9709) than the pseudo-first order R^2 values (0.4701 to 0.8949).

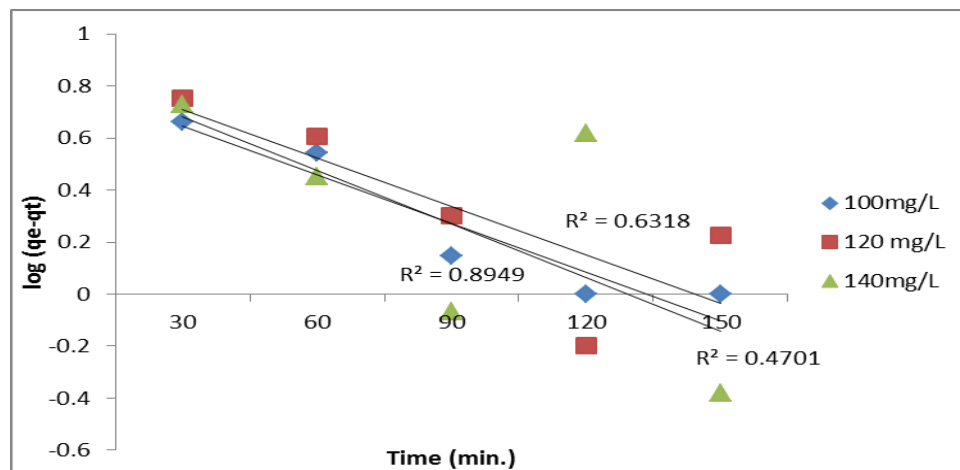


Fig. 9: Pseudo first order kinetics plots for adsorption of Pb(II) on to WASAC at varying Pb(II) concentration (pH = 3, T= 25⁰C, WASAC = 500mg).

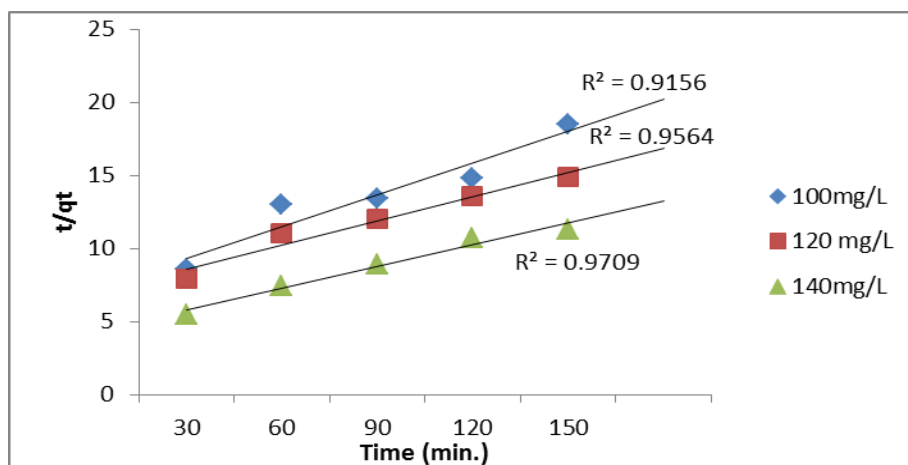


Fig. 10: Pseudo second order kinetics plots for adsorption of Pb(II) on to WASAC at varying Pb(II) concentration (pH = 3, T= 25⁰C, WASAC = 500mg).

CONCLUSION

In the present study, WASAC is used as an adsorbent for the removal of lead from aqueous solution. The studies shows that WASAC is a good, low cost adsorbent for the removal of Pb(II) from aqueous solution. The results clearly indicates that the percentage removal of Pb(II) decreases with an increase in initial Pb(II) concentration and pH. It was found that maximum adsorption achieved to be 81%.at an adsorbent dose 500mg and contact time 120 min with an initial Pb(II) concentration 100 mg/L and optimum pH 3.0. Langmuir isotherm was found better fitted with a high correlation coefficient ($R^2 = 0.9933$) than to freundlich isotherm with a correlation coefficient ($R^2 = 0.9288$). The rate of adsorption of Pb(II) on the WASAC was found to fit better with Pseudo second order kinetic model with a high correlation coefficient. The study clearly shows that WASAC is a good, cost effective, easily available and natural adsorbent for the removal of Pb(II) from waste water.

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