

Adsorption Studies on the Removal of Lead from Refinery Waste Water Using Bio-Surfactant Produced From E-Coli

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Abstract: The efficiency of biosurfactant produced from naturally occurring and abundant materials such as micro-organism and low cost substrates as a cost effective adsorbent for the removal of heavy metal ions from refinery waste water was studied. Rice husk obtained from Ufuma, in Orumba-North Local Government Area, Anambra State was activated and used as Mesoporous Activated Carbon unto which the biosurfactant was loaded. Both the thermal and chemical method of activation using heat and phosphoric acid was used to prepare the rice husk. The heavy metal studied is Lead. The removal efficiency of biosurfactant loaded (BS-MAC) and only MAC (control) was investigated under the same condition and it was found that BS-MAC is a better adsorbent than MAC. The biosurfactant was produced by the action of the micro-organisms (E-coli) on the low cost substrates (Orange waste). Proximate analysis was carried out on the low cost substrates and the refinery waste water to determine their properties. FTIR analysis was carried out on the biosurfactant produced for the investigation of the surface functional groups and also for the confirmation of removal of metal ions by the biosurfactant and the refinery wastewater was analysed after adsorption using Atomic Absorption Spectrophotometer (AAS) to further confirm the removal of lead. Batch adsorption studies were carried out by studying the effects of pH, dosage, and time on the adsorption process. Kinetic models such as Pseudo first-order, Pseudo second-order, Bhattacharya-Venkobachor and Power function model were used to fit the experimental data. The results showed that the Pseudo second-order best described the kinetics of the adsorption process. The calculated value of the amount adsorbed at equilibrium (q_e) from the Pseudo second-order kinetic model was found to be in good agreement with the experimental value.

Keywords: Adsorption, Orange waste, Bio-surfactant, Activated carbon, Lead, Kinetics.

1. INTRODUCTION

Increase in technology has positively affected the life of man on earth making life easier for man but, it also came with its own type of problems especially as regards pollution. It is difficult to separate industrial growth from pollution. Therefore, the excessive release of toxic organic and inorganic matter into the environment (which is pollution) due to industrialization has created a great global concern in recent years (Afshin et al, 2010). Pollution can occur in different ways especially as in water pollution, air pollution etc. Water pollution occurs when these harmful substances find themselves in water. Water pollution is as serious as air pollution because these harmful substances that are contained in industrial waste water when discharged with the waste water into water bodies cause serious danger to man, aquatic life, plants etc. While the petroleum refinery and petrochemical industries are most desirable for national development and improved quality of life, the unwholesome and environmentally unacceptable pollution effects of the waste from these industries are cause for worry. This is because in the process of converting crude oil into petroleum products (liquefied petroleum gas, naphtha, kerosene, diesel oil and residual oil) and petrochemical products (polypropylene, polyethylene), wastes of different kinds are generated.

Urban areas generally have a higher coverage of safe water than rural areas. Even within the urban area, there are variations in the quality of water as much of the water get contaminated in many different ways, through industrial effluent and untreated municipal sewage (Oluwande et al, 1993; Atubi, 2009a). Different methods that have been developed for the removal of these pollutants from wastewater include electrochemical oxidation, Precipitation, ion exchange resin (Afshin et al 2010), coagulation, solvent extraction, Liquid membrane permeation (Sofia et al, 2005), reverse osmosis (Al-Sultani and Al- Seroury, 2012) etc. Many problems that have been associated with most of the above methods include high cost, low efficiency, generation of toxic products and inability to regenerate the starting materials (Ehssan and Yehia, 2012). But biological treatment is very cost effective. Owing to these problems, emphasis has now been shifted to the use of adsorptive biological treatment for the removal of wastewater pollutants, which is now one of the most efficient technique

In recent years, special attention has been focused on the use of biosurfactant produced by the action of microorganism on natural waste materials which is very cheap, cost effective and at the same time helps to sanitize the environment. Biosurfactant is used as an alternative to replace the conventional adsorbents (Al- Sultani and Al- Seroury, 2012). Microorganism and natural waste materials (substrates) is readily available in large quantity and its potentials have not been clearly defined and put into proper use. Biosurfactant loaded MAC (Activated rice husk) is considered an effective and reliable method for the removal of dissolved pollutants in wastewater. Rice husk can be in granules or in powdered form (Djebbar et al, 2012).

Health effects of lead:

Lead is a soft metal that has known many applications over the years. It has been used widely since 5000 BC for application in metal products, cables and pipelines, but also in paints and pesticides. Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%). Foods such as fruit, vegetables, meats, grains, seafood, soft drinks and wine may contain significant amounts of lead. Cigarette smoke also contains small amounts of lead.

Lead can enter (drinking) water through corrosion of pipes. This is more likely to happen when the water is slightly acidic. That is why public water treatment systems are now required to carry out pH-adjustments in water that will serve drinking purposes. For as far as we know, lead fulfils no essential function in the human body, it can merely do harm after uptake from food, air or water.

Lead can cause several unwanted effects, such as:

- Disruption of the biosynthesis of haemoglobin and anaemia
- A rise in blood pressure
- Kidney damage
- Miscarriages and subtle abortions
- Disruption of nervous systems
- Brain damage
- Declined fertility of men through sperm damage
- Diminished learning abilities of children
- Behavioural disruptions of children, such as aggression, impulsive behaviour and hyperactivity

Lead can enter a foetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children.

Environmental effects of lead:

Not only leaded gasoline causes lead concentrations in the environment to rise. Other human activities, such as fuel combustion, industrial processes and solid waste combustion, also contribute. Lead can end up in water and soils through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints. It cannot be broken down; it can only be converted to other forms.

Lead accumulates in the bodies of water organism and soil organisms. These will experience health effects from lead poisoning. Health effects on shellfish can take place even when only very small concentrations of lead are present. Body functions of phytoplankton can be disturbed when lead interferes. Phytoplankton is an important source of oxygen production in seas and many larger sea-animals eat it. That is why we now begin to wonder whether lead pollution can influence global balances.

Soil functions are disturbed by lead intervention, especially near highways and farmlands, where extreme concentrations may be present. Soil organisms than suffer from lead poisoning, too. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains.

2. EXPERIMENTAL

2.1 Preparation of Activated rice husk:

The mesoporous activated carbon (MAC) was prepared from rice husk gotten from Ufuma, in Orumba-North Local Government Area Anambra State an agricultural by-product, using method followed by Ramani et al by a two stage process

1. Pre-carbonization
2. Phosphoric Acid Activation

The MAC was sieved to 600 micro- meter size and washed with hot water to remove the excess phosphorus compounds and dried at 110⁰C for 6 hrs to obtain the final product and stored until further use.

2.2 Preparation of Orange waste:

Orange waste collected in large quantity from waste bin and meshed to increase the surface area on which the micro-organism acts.

2.3 Physicochemical parameters and mineral composition of the substrates (orange waste):

Characterization of the substrates was also done to determine the properties of the substrates

Table.1 Physicochemical parameters and mineral composition of the substrate

Parameters	Orange waste
Moisture content(%)	73
Ash content(%)	0.5
Acid value(mg KOH/g of orange waste)	9.23
Saponification value(mg KOH/g of orange waste)	320.99
Iodine value(%)	18.15
Free fatty acid(%)	4.63
Peroxide value (O ₂ /Kg)	25.2
Cholesterol value (mg/g)	34.25
Carbon(%)	0.23
Hydrogen(%)	21.60
Nitrogen(%)	0.28
Elements (ppm)	
Zinc	0.862
Calcium	35.63
Copper	0.420
Iron	8.76
Chromium	Nil
Manganese	0.3

Table.2 Refinery Waste Water Analysis

Parameters	
pH	6.94
Turbidity NTU	1.3
Resistivity	3.0303
Alkalinity mg/l	165
Hardness mg/l	700
Calcium Hardness mg/l	174
Acidity mg/l	185.6
Conductivity us/cm	6.33
Total Dissolved Solid mg/l	120
Total Solid mg/l	180
Total Suspended Solid mg/l	69.1
Sulphate mg/l	304.51
Phosphorus mg/l	6.7464
Nitrate mg/l	7.5438
Chloride mg/l	600
Biological Oxygen Demand mg/l	13.4
Chemical Oxygen Demand mg/l	157.33
Elements(ppm)	
Cu	0.216
Fe	4.029
Al	0.332
Cr	0.063
Pb	0.571
Hg	0.203
Cd	0.212
Ca	20.915
Si	0.152
Mo	0.013
Ag	0.281
Mn	1.398
Co	0.131
Ni	0.740
Zn	4.606
K	72.258
Mg	8.246

2.4 Micro organism (E-Coli):

The microorganism was obtained in pathology department, University of Benin Teaching Hospital, Ogor Local Government Area in Edo State, Nigeria.

2.5 Production of Bio-surfactant:

A crude preparation of bio-surfactant was obtained. The culture broth obtained after a period of six days was filtered and centrifuged at 12,000g for 30mins to separate the cells from other debris. The supernatant was treated with three volumes of chilled acetone and allowed to stand for 12 hrs at 4°C. The precipitate thus obtained was washed with n-hexadecane, and collected by centrifugation.

2.6 Adsorption Studies:

Refinery waste water was gotten from Warri Refinery, in Warri, Delta State, Nigeria. Batch studies were carried out to study the effect of various parameters such as dosage, pH, and contact time on adsorption capacity of the biosurfactant loaded MAC produced. After adsorption, the solution was centrifuged and the absorbance measured at their wavelengths. The amount of equilibrium adsorption, q_e (ppml/g) was calculated as given in equation 1

$$q = \frac{(C_i - C_e)V}{m} \tag{1}$$

Where, C_i and C_e (ppm/L) are the liquid – phase concentrations of Lead at initial and equilibrium.

V is the volume of the solution (L) and

V is the volume of biosurfactant used (mls)

The percentage adsorbed % is as calculated in equation 2

$$\text{Percent adsorbed \%} = \left(\frac{C_i - C_e}{C_o} \right) \times 100 \tag{2}$$

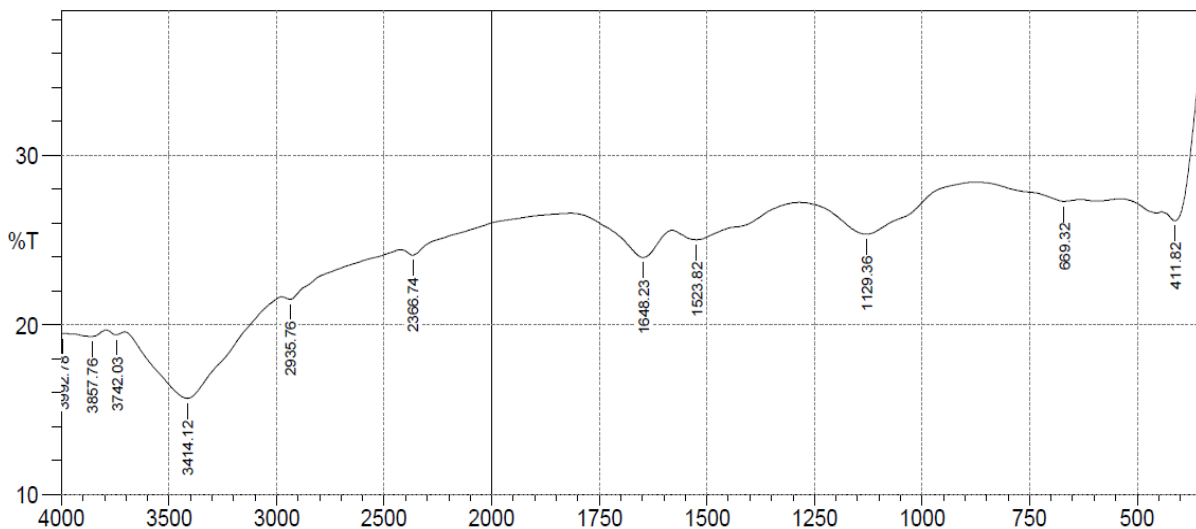
3. RESULTS AND DISCUSSION

3.1 Fourier Transform Infra-Red (FTIR):



FTIR ANALYSIS RESULT NARICT,ZARIA

FTIR- 8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER



No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	411.82	26.155	3.746	442.68	339.48	55.002	3.39
2	669.32	27.293	0.254	874.75	632.67	134.453	0.264
3	1129.36	25.356	2.328	1284.63	874.75	234.269	6.539
4	1523.82	25.023	0.867	1580.72	1284.63	173.442	2.127
5	1648.23	23.979	1.887	1815.08	1580.72	139.749	2.951
6	2366.74	24.113	0.529	2421.71	1815.08	360.218	0.196
7	2354.2	21.519	0.331	2975.3	2421.71	351.613	-1.663
8	3414.12	15.672	4.743	3706.34	2975.3	541.399	39.735
9	3742.03	19.414	0.005	3742.99	3706.34	26.018	0.001
10	3857.76	19.317	0.017	3868.37	3848.12	14.459	0.004
11	3992.78	19.481	0.002	4000.5	3989.89	7.536	0

FTIR studies were performed for the investigation of the surface functional groups in BFE and also for the confirmation of removal of metal ions by the biosurfactant.

The FTIR spectrum of BFE showed the presence of O-H stretching at 3452.7cm^{-1} , amides at 3390.01cm^{-1} , N-H bend at 1634.73cm^{-1} , C-Br stretch shows the presence of alkyl halides. The metal ion solutions were equilibrated individually with BS-MAC. The solution phase was separated from BS-MAC after the set time interval and analysed for lead by AAS. The heavy metal ions in aqueous solution before and after equilibrating with BS-MAC and MAC reveals that lead percentage removal is 99.71% and 45.1% respectively. This shows that BS-MAC is a better adsorbent than MAC.

3.2 Batch Adsorption Studies:

The batch adsorption was carried out to determine the effects of dosage, pH and time separately.

3.2.1 Effect of dosage:

The effect of dosage was studied for bio-surfactant dosages in the range of 2mls to 6mls for Lead. The results showed that, for Lead that as the bio-surfactant dosage increased, the percentage of adsorption also increased as can be seen from Figure 1.0. The increase in the percentage removal of heavy metal ions with the increase in biosurfactant dosage is due to the increased surface area with more active functional groups which also gives rise to more availability of more adsorption sites (Arivoli et al, 2009; Ladhe et al, 2011; Pragnesh et al, 2010). It was also observed that the amount adsorbed per unit mls of the adsorbent decreased as the adsorbent dosage increased. This decrease in unit adsorption with increasing adsorbent amount is mainly due to adsorption sites remaining unsaturated during the adsorption reaction (Bulut and Aydin, 2006). Similar results as above were obtained by many others such as Rashmi and Bani, (2003); Verma and Mishra, (2010) and Vikrant and Deshmukh, (2012).

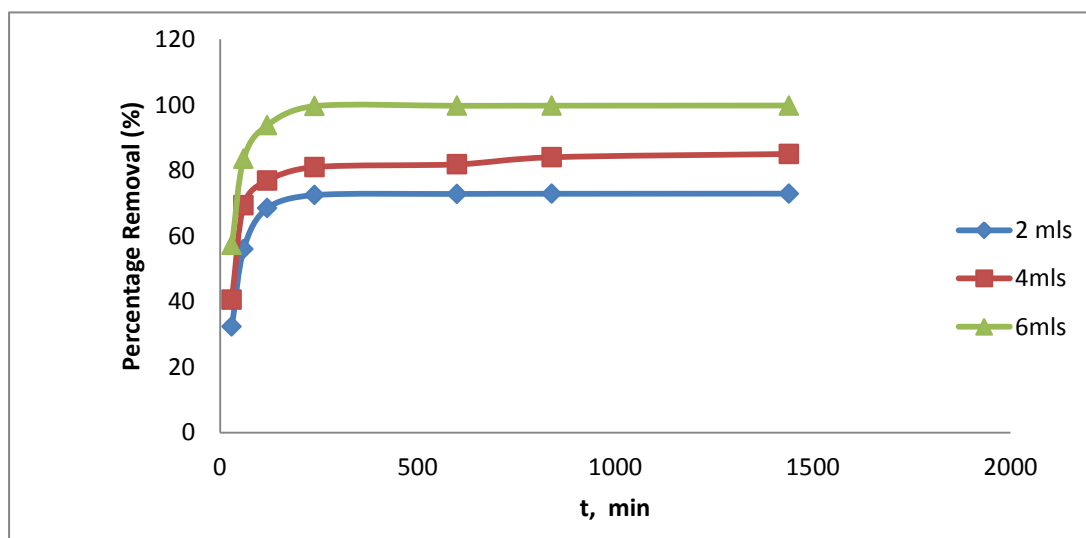


Fig 1.0 Effect of dosage on adsorption of Lead on biosurfactant produced E-coli

3.2.2 Effect of pH:

The percentage of adsorption of the heavy metal ion (Lead) was studied over the pH range of 6.0 to 8.0 and reported in Figures 2.0. The results indicated that the maximum removal of 99.71% Lead occurred at pH 8.0 and decreased as the pH decreased up to pH 6.0. This is due to the number of negatively charged adsorbent sites decreasing as the pH decreased. This causes the number of positively charged surface sites to increase which did not favour the adsorption of positively charged heavy metal ions due to electrostatic repulsion. Also, lower adsorption of Lead at acidic pH is due to the presence of excess H^+ ions competing with heavy metal ions for the adsorption sites of the adsorbent (Rajeshkannan et al, 2010). Similar results were obtained by Pragnesh et al, (2010), Rajeshkannan et al, (2010) and Venckatesh et al, (2010). But for the adsorption of Lead using only activated rice husk which is used as a control, it was found that at pH 7, maximum removal of 45.1% was obtained followed by pH 8 and then pH 6. This is because the active sites in the activated rice husk

are protonated at low pH (pH 6) resulting in retardation of metal ions by them, accounting for poor removal of heavy metal ions in aqueous solution. At neutral pH, the active sites are active enough to chelate the heavy metal ions resulting in the maximum removal of heavy metal ions in aqueous solutions.

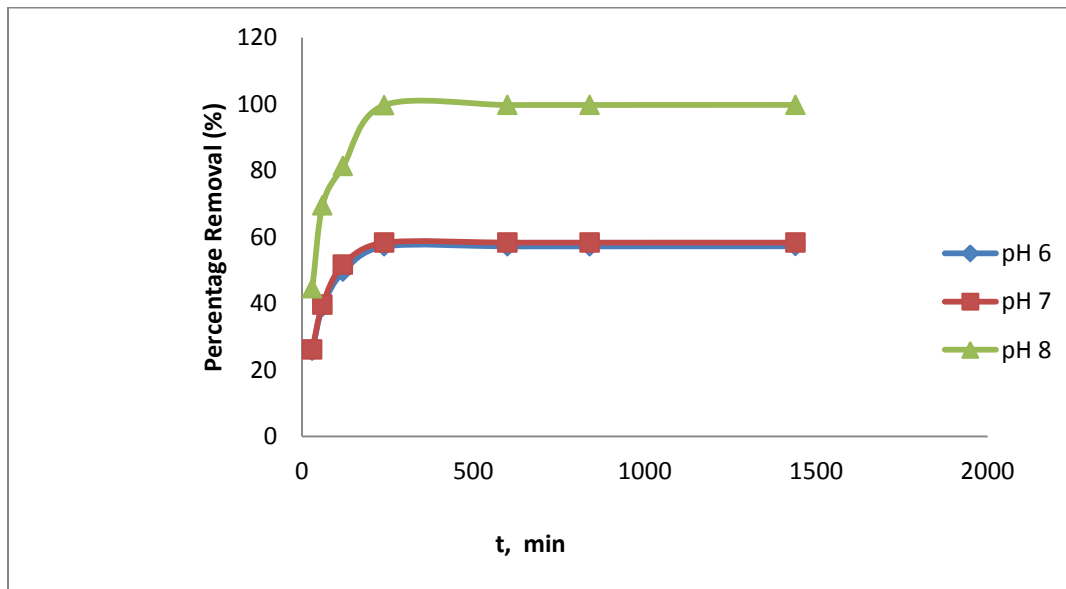


Fig 2.0 Effect of pH on adsorption of Lead on E. coli produced biosurfactant

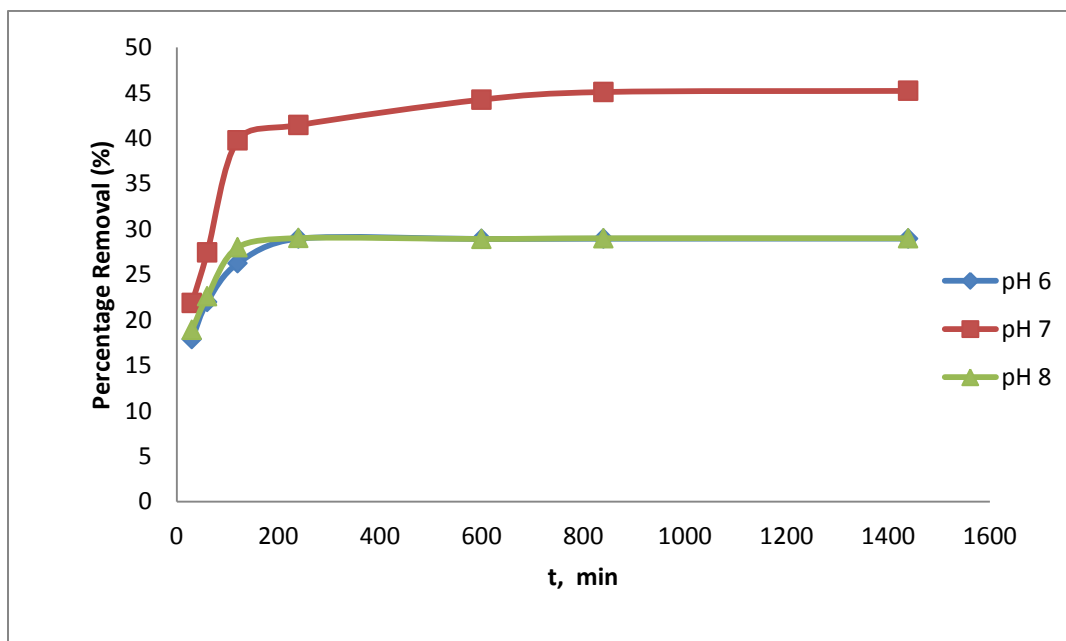


Fig 3.0 Effect of pH on adsorption of Lead on Activated Rice Husk

3.2.3 Effect of time:

The result showed that as the time increased, the percentage of Lead adsorbed increased until equilibrium was reached at about 240mins. The initial rapid adsorption was due to the availability of the charged surface of the adsorbents for the adsorption of Lead and Chromium (Goswami and Ghosh, 2005). The increase in the extent of removal of the heavy metal ions with increasing time is because adsorbate generally formed monolayer on the surface of the adsorbent. Thus, the removal of heavy metal ions from aqueous solution is controlled by the rate of the transport of the adsorbate species from the outer sites to the interior sites of adsorbent. Many other researchers that reported a similar trend include Vikrant and Deshmukh, (2012), Tabrez et al, (2004) and Verma and Mishra, (2010).

3.3 Kinetic Studies:

Only one kinetic models best fits this adsorption process as explained below:

3.3.1 Pseudo second-order kinetic model

The pseudo second order kinetic model was by Ho and Mckay and expressed below as (Srihari and Ashutosh, 2009).

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{3}$$

Integrating the above equation between the boundary condition of t = 0 to t = t and q_t = 0 to q_t = q_t will yield

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t \tag{4}$$

which on linearizing will yield

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

Where,

K₂ = rate constant of the pseudo second order adsorption (g/ppmlmin)

q_e = equilibrium adsorption capacity (ppml/g).

Hence, the plot t/q_t versus t in Fig 4 was used to demonstrate the pseudo – second order model and the constants evaluated. At different dosages, the plot of t/q_t versus t was used to demonstrate the pseudo-second order.

The correlation coefficient R² has very high values of 0.999 for the adsorption of Lead on the adsorbent. Equally, the values of the calculated equilibrium adsorption capacity (q_e) 1.942 ppml/g is very close to the experimental values. Hence, the adsorption of Lead on the adsorbent is best followed by the pseudo second – order kinetic model.

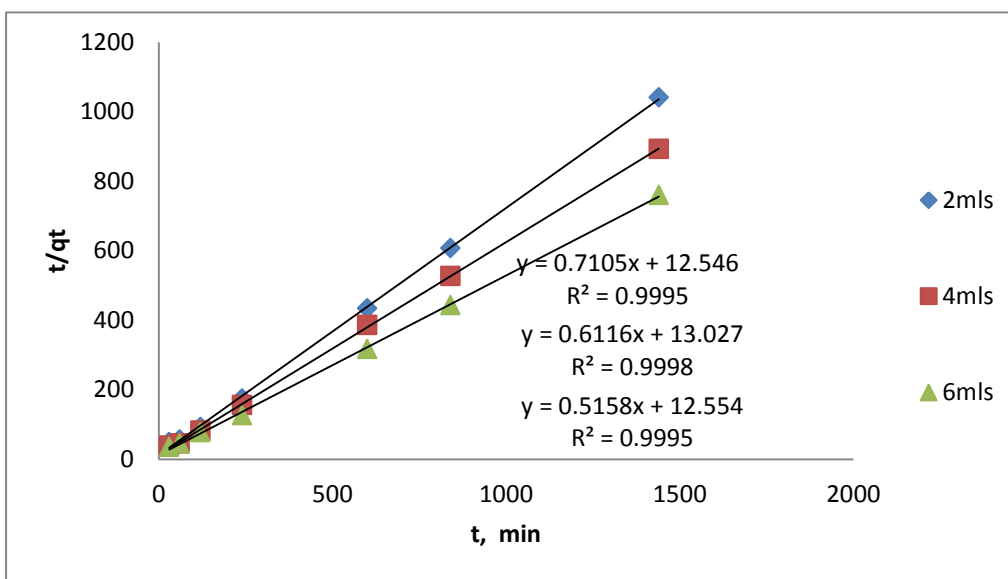


Fig 4.0 Pseudo second-order plot for the adsorption of Lead on Biosurfactant produced from E-coli

4. CONCLUSION

This study showed that Lead can effectively be adsorbed from aqueous solution using BS-MAC. The batch study shows that the percentage of Lead adsorbed depends on pH, dosage and time. The maximum time for significant removal was 240 minutes while the pH for most effective removal was 8. BS-MAC is a better adsorbent than MAC. Kinetic study indicated that the pseudo second-order best described the adsorption process. Statistical analysis confirms that Intra-particle diffusion is not the sole rate-controlling process. The production of biosurfactant helps in environmental sanitation and the use of biosurfactant in the treatment of waste water is cost effective.

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