Abstract

The adsorption of lead (II) ions from aqueous solution has been investigated on formaldehyde polymerized orange peel (FPOP), at room temperature. The biosorbent is characterized by FTIR. The biosorption experiments were carried out in batch system as a function of pH, contact time, adsorbent dose, temperature and initial concentration of Pb (II) ions. Biosorption was pH dependent and maximum removal of Pb (II) was obtained at 5.0. The equilibrium was established in 120 min. Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich adsorption isotherm models were applied to the equilibrium data. The equilibrium data are satisfactorily fitted in the order of Langmuir > Freundlich > Tempkin > Dubinin-Radushkevich. The maximum biosorption capacity was 29.9 mg g\(^{-1}\). The kinetics of Pb (II) ions adsorption was very well described by pseudo-first order and pseudo–second order kinetic models but fitness is high with later with high \(R^2\) values exceeding 0.999. The result of study showed that the orange peel can be efficiently used as low cost alternative for the removal of divalent lead from industrial waste water.

1. INTRODUCTION

Toxic heavy metal contamination of industrial waste water is an important environmental problem. Many industries, such as automotive, mining, electric cable manufacturing, battery manufacturing, metal finishing, electroplating, tannery, steel and textile industries, release various concentration of metals like lead, copper, nickel etc. through waste water. Their accumulation in living tissues through the food chain causes a serious health hazard; like mucosal irritation, central nervous system irritation, brain damage, and cancer etc. so strict environmental protection legislation and public environmental concerns drive the search of novel techniques to remove heavy metals form industrial waste water. Although many techniques have been developed, some of that are reverse osmosis, ion-exchange, chemical precipitation etc. however these are expensive or difficult to implement.
Adsorption is one of the most respective methods that it has been successfully applied for Pb (II) ions removal from waste water; due to its low cost, high efficiency and ease of operation. Removing of metal from waste water required the use of efficient biosorbent material. Many agricultural based waste materials have been employed for treatment of lead like rice husk, sea weeds, hazelnut, peanut hulls etc.

In the present study, the ability of orange peel for the removal of Pb (II) ions from aqueous solution is investigated using batch biosorption procedure at room temperature. Experimental parameters such as pH, initial Pb (II) ion concentration, contact time, dose of biosorbent and temperature on biosorption capacity were studied.

2. EXPERIMENTAL:

2.1 Biosorbent material

The orange peel have been used as a biosorbent material, which was obtained from the agricultural field of Shajapur, M.P. India were washed repeatedly with demonized water in order to remove dust and other impurities and then dried at 40°C for 24 hrs. It was crushed, to obtain fine power. Then these material treated by formaldehyde to get the formaldehyde polymerized orange peel (FPOP).

2.2 Chemical Treatment

Treatment is given to orange peel according to method as described by B.F. Neoline et al. 2 parts of powdered orange peel was treated with 20 parts of 0.2 N H₂SO₄ and 5 parts of 39% HCHO. The
mixture was heated in water bath at 60 °C for 6 hrs and stirred vigorously. The FPOP thus obtained was filtered and washed to remove excess of acid and dried at 60 °C these FPOP is used for all further adsorption experiments.

2.3 Characterization of FPOP

The FTIR spectra are used to identify the characteristic functional group on the biosorbent. The cation exchange capacity was determined by the column process using 1.0 M NaNO₃ as the eluent at a flow rate of 0.5 ml/min. Absorbance was measured with a Perkin-Elmer model A-analyst-100 atomic absorption spectrophotometer. A pH-meter (ELICO-LI-612) and shaker (REMI- Electronic equipment) were used for pH adjustment and shaking respectively. Characterization of functional group has been done by FTIR (Thermo-scientific Nicolet-360) spectrometer.

2.4 Batch experiment

Batch experiments were conducted in Stoppard reagent bottle of 250 ml capacity. In to each bottle 100 ml of synthetic solution at pH-5, was added together with an accurately weighted amount (0.1-2 gm) adsorbent. A series of such bottles were shaken at 200 rpm at 25 °C. The sample was filtered to remove any fine particle the remaining Pb (II) ions were determined by AAS method. Triplicate determination was made for each determination and their means value computed for quantity assurance.

3. RESULTS AND DISCUSSION

3.1 Effect of contact time

Experimental studies were carried out at temperature 25 °C with varying initial metal ion concentration of Pb (II) 10, 50, 100 mg/L using 1.0 gm adsorbent dosage at pH 5.0. It is clear from Fig.1 that the Pb (II) ion removal increased with contact time and was rapid for the first 50 min and thereafter it proceeded at a lower rate and finally attained saturation. Equilibrium adsorption was stabilized within 120 min for all initial Pb (II) ion concentration. The trend in adsorption of Pb (II) suggests that the binding may be through the interaction with functional groups located on the surface of FPOP. The removal of Pb (II) ions of concentration 10, 50 and 100 mg/L at contact time 120 min. were 92.1%, 84.86% and 77.99% respectively.
3.2 Effect of adsorbent dose

The sorption of Pb (II) ions increased with increasing the amount of sorbent from 0.1 to 2.0 gm. It is clear from Fig.2 that with the increase in the amount of sorbent, the available sites for the sorption are increased. Therefore, at constant concentration of pollutant metal ion the rate of sorption was greater at higher sorbent dose. This trend is expected because as the adsorbent dose increases the number of adsorbent particles increases and thus more Pb (II) is attached to their surface. The adsorption percentage for Pb (II) ions increased from 55.98 to 96.9, 15.38 to 93.36 and 11.99 to 88.97% for 10, 50 and 100 mg/L initial feed concentration respectively with the increase in the adsorbent doses from 0.1 to 2.0 g/L at constant temperature 25 °C and pH 5.

Fig. 2:- Effect of Dose of adsorbent on percentage removal of Pb (II) ion by FPOP
3.3 Effect of pH

Solution pH plays a vital role in heavy metal biosorption. The speciation of metal in solution is pH dependent and at the same time, the state of chemically active sites is changed by the variation in solution pH. In order to determine the optimal value, pH of solution was varied from 1±0.1 to 8±0.1. As depicted in Fig. 3, the maximum biosorption of lead occurred in the pH range of 3–7. The increase in metal removal capacity at higher pH may also be attributed to the reduction of H\(^+\) ions which compete with Pb (II) ions at lower pH. The speciation of lead is pH dependent. At pH of 2–5 lead always exclusively exists as Pb (II), above pH of 6, it is hydrolyzed to PbOH\(^+\) and Pb (OH)$_2$. The predominant sorbing forms of lead are Pb (II) and PbOH\(^+\) which occurred in the pH range of 4–7. This was the reason for higher removal of lead in the pH range of 4–7. At pH higher than 7, precipitation of lead occurred and removal due to biosorption was reduced.

![Fig. 3: Effect of pH on percentage removal of Pb (II) ion by FPOP](image)

3.4 Effect of temperature

The temperature is an important parameter in the context of adsorption on solid phase and has two major effects on the adsorption process. Increase in the temperature is known to increase the rate of the diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to decrease in the viscosity of the solution. Experiments were performed at different temperature (30, 35, 40, 45, 50, 55 and 60 $^\circ$C), keeping the other parameters constant. Equilibrium time for 30, 35, 40, 45, 50, 55 and 60 $^\circ$C was also found to be 120 min; it
indicated in the fig 4 that the equilibrium time was independent of temperature. These results also showed the endothermic nature of adsorption.

Fig. 4:- Effect of Temperature on percentage removal of Pb (II) ion by FPOP

3.5 Effect of initial metal ion concentration

The experimental studies were carried out with varying initial metal ion concentration of Pb (II) ions, ranging from 10 to 500 mg/l using 1 g of FPOP dose at pH 5.0: It is clear from the figure that the equilibrium sorption capacity of the biomass for Pb (II) ions increased while the percentage adsorption decreased with a rise in initial metal ion concentration. The increase in loading capacity is probably due to a high driving force for mass transfer [8]. However the percentage adsorption of Pb (II) ions on FPOP was decreased from 89.36 to 42. This may be attributed to lack of sufficient surface area to accommodate much more metal ion available in the solution.

Fig. 5:- Effect of Initial metal ion concentration on percentage removal of Pb (II) ion by FPOP
3.6 Isotherm studies

Four adsorption isotherm models \cite{17} were used in present work namely Freundlich, Langmuir, Dubinin-Radushkevich and Tempkin.

3.6.1 Freundlich isotherm

The well-known Freundlich expression is represented in Eq. (1):

\[
q_e = k C_e^{1/n} 
\]

This equation is conveniently used in the linear form by taking the logarithm of both side as:

\[
\ln q_e = \ln k + \frac{1}{n} \ln C_e 
\]

Where,

- \( q_e \) is the amount of metal ions adsorbed per unit volume of adsorbent (mg/g)
- \( C_e \) is the equilibrium aqueous metal ions concentration (mg/l).

![Langmuir Adsorption isotherm](image)

Fig.6 :- Langmuir adsorption isotherm for the removal of Pb (II) ion by FPOP

3.6.2 Langmuir isotherm

The well-known Langmuir expression is represented in Eq. (3):

\[
q_e = \frac{b C_e}{1 + b C_e} 
\]

The linear form of the equation is as follows:
\[ \frac{1}{q_e} = \frac{1}{\theta^0 b} \left( \frac{1}{C_e} \right) + \frac{1}{\theta} \quad (4) \]

Where,

- \( q_e \) is the amount of metal ion adsorbed at specified equilibrium (mg/g),
- \( C_e \) is the equilibrium concentration of Pb (II) ions in test solution (mg/l),
- \( \theta^0 \) and \( b \) are the Langmuir constants related to adsorption capacity and energy of adsorption.

The isotherm constants along with their correlation coefficient are reported in Table 1.

![Ferudich adsorption isotherm](image)

**Fig. 7:** Freundlich adsorption isotherm for the removal of Pb (II) ion by FPOP

### 3.6.3 Dubinin-Radushkevich (D-R) adsorption isotherm

D-R isotherm model is more general than the Langmuir isotherm. The linear form of D-R adsorption isotherm is expressed in Eq. (5):

\[ \ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5) \]

Where,

- \( \beta \) is a constant related to the mean free energy of adsorption per mole of the adsorbate (mo\(^2\) kJ/mol),
- \( \varepsilon \) is the theoretical, and \( \varepsilon \) is the Polanyi potential, which is equal to \( RT \ln (1+(1/C_e)) \),

where \( R \) (J/mol K) is the gas constant and \( T \) (°K) is the absolute temperature.

\[ E = \frac{1}{\sqrt{2\beta}} \quad (6) \]
3.6.3 Tempkin adsorption isotherm

Tempkin and Pyzhev (1940) considered the effect of indirect adsorbate-adsorbate interactions on adsorption isotherms. The Tempkin isotherm is expressed as

\[ q_e = B_T \ln A_T + B_T \ln C_e \tag{7} \]

Where, \( BT = (RT/bT) \), \( T \) is absolute temperature (K), \( R \) is gas constant (8.314 J/mol k). The constant \( bT \) is related to the heat of adsorption. The values of \( BT \) and \( AT \) were determined from linear plot of \( qe \) versus \( \ln Ce \).

Fig. 8: Dubinin-Radushkevich adsorption isotherm for the removal of Pb (II) ion by FPOP

Fig. 9: Tempkin adsorption isotherm for the removal of Pb (II) ion by FPOP
Table 1
Freundlich, Langmuir, Dubinin-Radushkevich (D-R) and Tempkin isotherm constants and correlation coefficient for the adsorption of Pb(II) ions by FPOP at different temperature.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Temperature (°C)</th>
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<td></td>
<td></td>
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<td>35</td>
<td>40</td>
<td>45</td>
<td>50</td>
<td>55</td>
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<tr>
<td>Freundlich</td>
<td>k_f</td>
<td>0.697</td>
<td>0.735</td>
<td>0.789</td>
<td>0.859</td>
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<td></td>
<td>n</td>
<td>1.307</td>
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<td></td>
<td>R²</td>
<td>0.999</td>
<td>0.997</td>
<td>0.996</td>
<td>0.995</td>
<td>0.999</td>
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<tr>
<td>Langmuir</td>
<td>q_e (mg/g)</td>
<td>12.099</td>
<td>15.442</td>
<td>18.553</td>
<td>22.085</td>
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<td>b (L/mg)</td>
<td>0.119</td>
<td>0.091</td>
<td>0.070</td>
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<td>R²</td>
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<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
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<td>Dubinin-Radushkevich</td>
<td>Q_m (mg/g)</td>
<td>1.472</td>
<td>1.281</td>
<td>1.25</td>
<td>4.684</td>
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<td>β (mol² kJ⁻²)</td>
<td>19259.76</td>
<td>20461.6</td>
<td>23284</td>
<td>27083</td>
<td>32180</td>
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<td>R²</td>
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<td>0.974</td>
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<td>0.976</td>
<td>0.973</td>
<td>0.970</td>
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<td></td>
<td>E (kJ/mol)</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.002</td>
<td>0.002</td>
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<tr>
<td>Tempkin</td>
<td>B</td>
<td>699.07</td>
<td>682.596</td>
<td>659.909</td>
<td>639.558</td>
<td>590.229</td>
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<td>A (L/g)</td>
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<td>0.005</td>
<td>0.0002</td>
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<td></td>
<td>R²</td>
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<td>0.998</td>
<td>0.998</td>
<td>0.996</td>
<td>0.996</td>
<td>0.979</td>
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3.7 Sorption kinetics

Sorption kinetics studies are significant in the study of biosorption since they not only provide valuable insights into the reaction pathways, but also describe the solute uptake rate which in turn controls the residence time of sorbate at the solid-liquid-interface.

\[ q_t = (C_0 - C_f) \frac{V}{m} \]  \hspace{1cm} (8)

Where, \( C_0 \) and \( C_f \) are initial and final metal ion concentration (mg/L) respectively. \( V \) is volume of solution (L) and \( m \) is FPOP weight in dry form (g).

3.7.1 Pseudo first order kinetics

The Pseudo first order equation of Lagergren and Kinglike is generally expressed as follows

\[ \frac{dq_t}{dt} = K_1(q_e - q_t) \]  \hspace{1cm} (9)

Where,

\( q_e \) and \( q_t \) are adsorption capacity at equilibrium and at time \( t \), respectively (mg/g) and \( k_1 \) is the rate constant of pseudo first order sorption (min\(^{-1}\)).

Fig. 10: Pseudo I order rate reaction for the removal of Pb (II) ion by FPOP
3.7.2 Pseudo second order kinetics

The pseudo second order equation on the sorption capacity of the solid surface and is expressed as

\[
\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{10}
\]

Where, \( q_e \) and \( q_t \) are adsorption capacity at equilibrium and at time \( t \), respectively (mg/g) and \( k_2 \) is the rate constant of pseudo second order sorption (min\(^{-1}\)). The various kinetic model constants and their corresponding correlation coefficient are reported in Table 2.

![Graph](image_url)

Fig. 11: Pseudo II order rate reaction for the removal of Pb (II) ion by FPOP

<table>
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<th>Type</th>
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<th>50 mg/L</th>
<th>100 mg/L</th>
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<td>Pseudo I Order</td>
<td>( q_e ) (mg/g)</td>
<td>1.694</td>
<td>3.249</td>
<td>3.391</td>
</tr>
<tr>
<td></td>
<td>( K_f )</td>
<td>0.051564</td>
<td>0.03314</td>
<td>0.015522</td>
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<tr>
<td></td>
<td>( r^2 )</td>
<td>0.9703</td>
<td>0.98144</td>
<td>0.95493</td>
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</table>

Table 2
Pseudo First order and Pseudo second order kinetic parameters obtained by linear regression method at different initial Pb (II) ion concentration.
Pseudo II order

<table>
<thead>
<tr>
<th>qe (mg/g)</th>
<th>k (g/mg min)</th>
<th>h (mg/g min)</th>
<th>r²</th>
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</thead>
<tbody>
<tr>
<td>0.970233</td>
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<td>4.791337</td>
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<td>0.298291</td>
<td>0.9991</td>
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<td>10.39393</td>
<td>0.002247</td>
<td>0.242721</td>
<td>0.98998</td>
</tr>
</tbody>
</table>

3.8 FTIR analysis

The FTIR graph of TFS unloaded untreated, FPOP unloaded and FPOP loaded with Pb (II) ion are shown below respectively. FTIR spectra of untreated TFS exhibit peaks on 445.9, 423.7, 1469.81, 1504.4, 1537.68, 1556.43, 1633.33, 1731.35 corresponding to the presence of various functional group viz. >C=0, C=O str., 0-H vib. A very broad spectrum occurs at 3500 cm⁻¹ which corresponds to –OH str. FTIR spectra of FPOP exhibits peak at 401.49, 1556.62, 1650.74, 1659.87, 1693.7, 1703.63 and 3525.76. There is change in peak of FPOP Pb loaded graph thus indicating the adsorption of Pb (II) ion at adsorbent surface.

4. CONCLUSIONS

In the present study, batch adsorption experiments for the adsorption of Pb (II) ions from aqueous solutions have been carried out using Orange peel treated with formaldehyde (FA). The adsorption Characteristics have been examined at different contact times and initial Pb (II) ion concentrations, pH values, temperatures and different adsorbent dosage levels. The obtained results can be summarized as follows:

i. The adsorption rate of Pb (II) ions was very fast initially, and about 40% of total Pb (II) was removed within min 30. Thereafter, the adsorption capacity increased slowly with the contact time before reaching a plateau value after the contact time of 2h, and then remained constant.

ii. Generally, removal of Pb (II) ions by (FPOP) increased with an increase in the pH of the adsorbate solution. The optimum pH for Pb (II) removal is 5.0.

iii. Increase in adsorbent dosage led to increase in Pb (II) removal but decrease in adsorption capacity.
iv. Kinetic studies indicated that the sorption tends to follow pseudo second-order kinetics for the range of concentration studied for the entire sorption period. Adsorption of Pb (II) ions by FPOP was found to follow the pseudo-second-order model.

v. Langmuir adsorption model was better fitted for the adsorption of Pb (II) ions than Freundlich, Temkin and Dubinin-Radushkevich isotherms. The highest monolayer sorption capacity obtained as 29.078 mg g\(^{-1}\).

vi. The adsorption capacities of the adsorbents for the removal of Pb(II) have been compared with other adsorbents reported in the literature.

vii. Studies on batch adsorption indicate that FPOP has efficient adsorption capacity for Pb(II) ions and its use may significantly lower the cost of water treatment.

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5. References