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Equilibrium and Kinetic Studies of Adsorption of Lead using Low Cost Adsorbents

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Abstract

Background: Anthropogenic activities are major source of water pollution, particularly, because of haphazard dumping of heavy metals which get accumulated through trophic levels posing a severe risk to the surroundings. The removal of heavy metals from wastewater is, thus, very significant. **Objective:** The objective of the present study is to use rice husk, tea waste and orange peel for removal of Pb (II) ions by adsorption and to develop equilibrium and kinetic studies data for the same. **Method:** The batch process of adsorption was used and the concentration of lead adsorbed was measured titrimetrically. **Findings:** The maximum removal efficiency has been observed as 88% in tea waste and 80% in rice husk and orange peel. The equilibrium data obtained at optimized conditions for all the metal ions studied has been subjected to the isotherm models used for adsorption, namely, Langmuir and Freundlich. Further, to examine the kinetics for adsorption of Pb (II) ions on the adsorbents under study, pseudo first order and second order equations have been analysed. Thus, it was concluded that the utilization of low cost waste materials for treating wastewater using adsorption is effective, eco-friendly, locally available causing no pollution along with solving the problem of waste disposal.

Keywords: Adsorption, Adsorbent, Isotherm, Kinetics, Pb (II), Removal.

1. Introduction

As far as environment and human health are concerned, pollution due to improper waste water disposal has been a major issue. The indiscriminate usage of chemicals, pesticides, fertilizers etc. has lead to the worsening condition of the environment. Heavy metals are of utmost concern among these pollutants, because these toxic pollutants do not undergo chemical or biological degradation and can build up in living tissues and bio-concentrate on moving up in the food chain. The presence of one such heavy metal i.e. lead in potable water is of utmost concern because of its high toxicity and persistence. Lead ion is introduced into water stream through a range of industrial applications. Consumption of lead can lead to cognitive mutilation, disturbance in behaviour, renal damage and is lethal to reproductive as well as nervous system etc. Also, Lead is the only heavy metal causing anaemia. Therefore, the need for proper treatment for wastewater containing heavy metals is emphasized.

To reduce the concentration of heavy metals, various processes like precipitation using lime, ion exchange, adsorption, membrane process have been used[1]. The above discussed methods are normally quite expensive. Adsorption is being used on a large scale by researchers throughout the world for the elimination of these heavy metals from water and the most frequently used adsorbent is Activated carbon. Regardless of its widespread usage in wastewater treatment, activated carbon is a costly material. This called for the development of low-cost adsorbents made from agricultural

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waste, construction waste, food waste etc. Many previous studies illustrate the use of bio-sorbents to eliminate heavy metals, from wastewater[2]. This technology has shown great potential for the treatment of wastewater as it has many advantages like low cost, easy operability, abundant availability etc. over the conventional methods.

The aim of the present effort is to explore the likely use of easily available adsorbents namely; rice husk, spent tea leaves and orange peel to adsorb lead from aqueous solution. All these adsorbents are easily available, commercially viable, economical and eco-friendly.

2. Experimental

2.1 Sample Preparation

Preparation of synthetic water samples containing lead was done by using lead nitrate. A stock solution having a concentration of 1000 mg/L and a strength of 1M was prepared. The further dilution of various required concentrations was done using the stock mixture.

2.2 Adsorbent Preparation

Rice husk, Tea residue and Orange peel were continuously washed using distilled water till the water became colourless. After that, the material was sun dried and the adsorbents were crushed into a fine powder and sieved to a ground size.

2.3 Method

The experiments were conducted using batch process in conical flasks having a volume of 250 mL with the sample volume as 100 mL. The samples were mixed using a flask shaker at 100 rpm and experimentation was done at room temperature. The maximum contact time of 150 minutes was provided. The quantity of lead adsorbed was recorded with the help of titration as per the technique given[3]. The experiments were conducted to find the relation of Dose of Adsorbent(0.4-1.2g/100 mL), pH (2-6), initial lead ion concentration (20-100 mg/L) and time of contact (30-150 min) with removal efficiency.

The quantity of lead adsorbed was calculated using equation 1 as follows:

$$\% \text{ adsorption} = \frac{(C_o - C_e)}{C_o} X\, 100 \quad (1)$$

Where, C_o and C_e are the initial and final concentrations of lead ions, respectively.

The quantity of lead adsorbed/ Kg of the adsorbent was calculated using the equation as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where $\mathbf{q_e}$ is the amount of adsorbed lead ion on the adsorbent, m is the weight of adsorbent, **V** is the volume of lead ion solution, $\mathbf{C_o}$ is the initial lead ion concentration, and $\mathbf{C_e}$ is the final lead ion concentration.

The isotherm studies were done with the help of Langmuir and Freundlich isotherms. For Langmuir isotherm, the graph was plotted linearly between (1/q) and (1/C) with ($1/q_e$ b) as the slope and (1/qe) as the constant as shown in figure. 5. For Freundlich isotherm, the graph was plotted between log q and log C with log K as constant and having a slope of 1/n using equation 4.The graph shows a linear variation.

The kinetics studies using pseudo first and second order mathematical relations were performed. For the first order, the linear graph was plotted between log (q_e-q_o) and time showing a correlation of the log of adsorbed amount of metal ion with respect to time using equation 5. For pseudo second order, the graph was plotted between t/qo and time as shown in equation 6. It shows a linear variation. It gives the correlation of final concentration with respect to time over a time period.

3. Results and Discussion

3.1 Characteristics of Adsorbent

Surface area is a key factor in finding out the suitability of material for removing heavy metals from solution. It adds up to the acclimatization of the metal ion on the surface of adsorbent. Surface area was found out using the BET (Brunauer–Emmett–Teller) N_2 technique. In order to have better idea about the surface functional groups available on the surface of the adsorbents under study, their IR spectra were recorded and are shown in Figure 1, 2, 3, 4, 5 and 6. The Fourier Transform Infrared Spectroscopy (FTIR) analysis also gives knowledge about the surface area available for adsorption. The Surface area of rice husk, spent tea leaves and orange peel was found to be 14.494 m^2/g, 18.818 m^2/g and 16.736 m^2/g respectively, indicating that the spent tea leaves has maximum surface area, thus, capable of accommodating maximum number of metal ions.

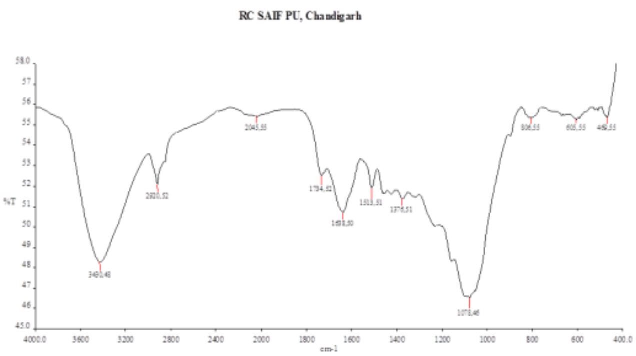

Figure 1. FTIR Spectrum of RH before adsorption.

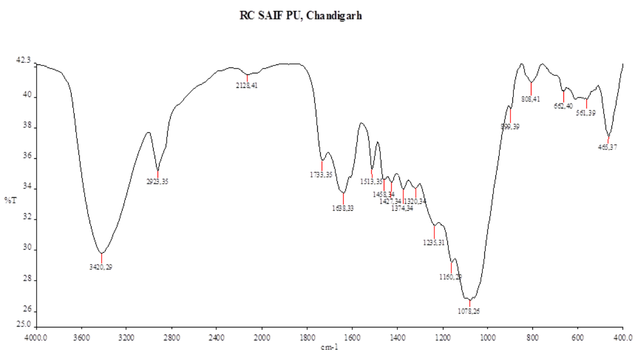

Figure 2. FTIR Spectrum of RH after adsorption.

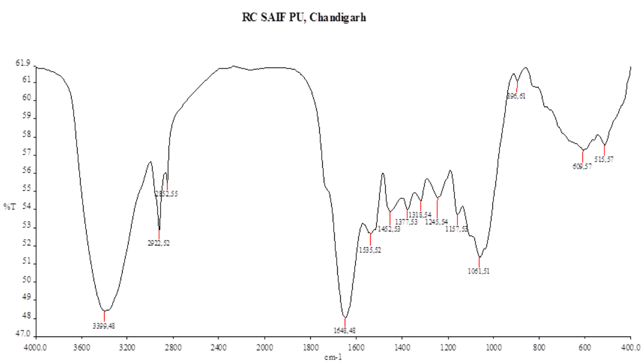

Figure 3. FTIR Spectrum of TW before adsorption.

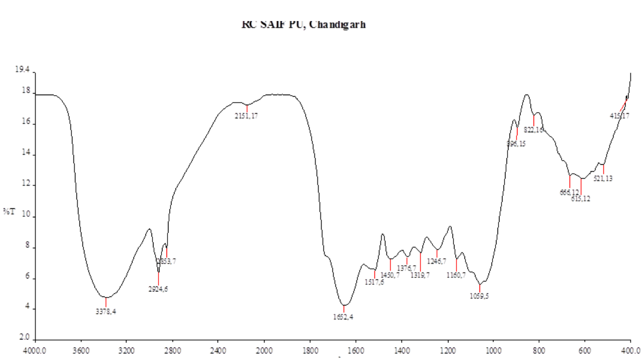

Figure 4. FTIR Spectrum of TW after adsorption.

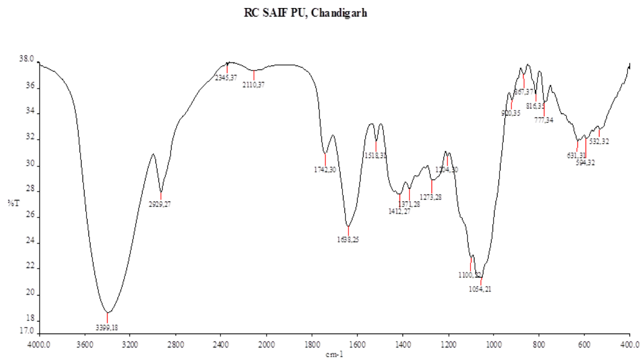

Figure 5. FTIR Spectrum of OP before adsorption.

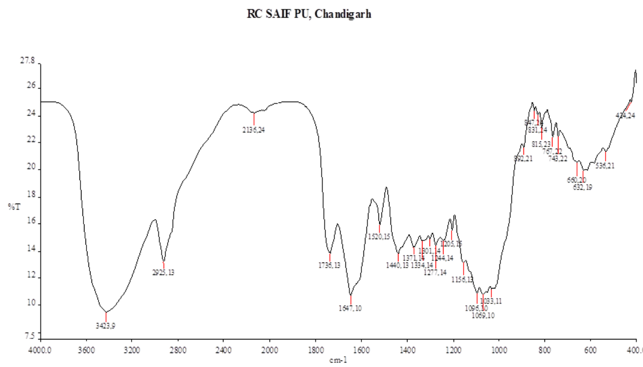

Figure 6. FTIR Spectrum of OP after adsorption.

3.2 Effect of pH

In case of the pH, the effectiveness of lead removal increases as the pH increases. The highest removal efficiency attained is 80% for Rice husk and Orange peel and 88% for Spent tea leaves as shown in Figure 7. The adsorption is lesser in acidic range because there is electrostatic repulsion between the adsorbent and lead ions due to high positive charge density between the two, resulting in lower amount of adsorption. As the pH increases, electrostatic repulsions decrease causing increase in adsorption[4].

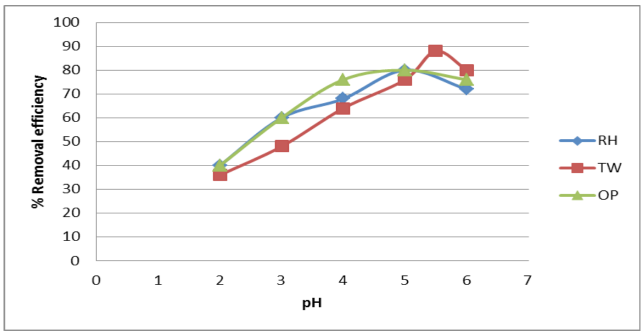

Figure 7. pH v/s Efficiency for adsorbents.

3.3 Effect of Adsorbent Dose

With increasing adsorbent dose, the removal efficiency increases due to greater number of exchangeable sites i.e. Surface Area. The graph Figure 8 shows almost similar results for all the adsorbents. The optimum adsorbent dose is 1g for all the adsorbents. Further addition of adsorbent does not have any change in the removal efficiency.

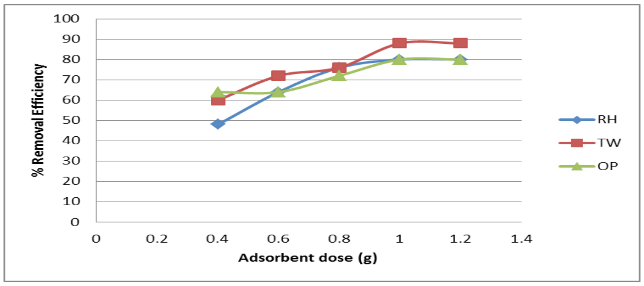

Figure 8. Adsorbent Dose v/s Efficiency for adsorbents.

3.4 Effect of Contact Time

The contact time also controls the process of adsorption. As the contact time increases, the removal efficiency increases until it reaches the equilibrium. After that, it remains constant. As shown in Figure 9, the curves for rice husk and spent tea leaves show almost linear trend. Adsorption due to orange peel shows little variation w.r.t contact time.

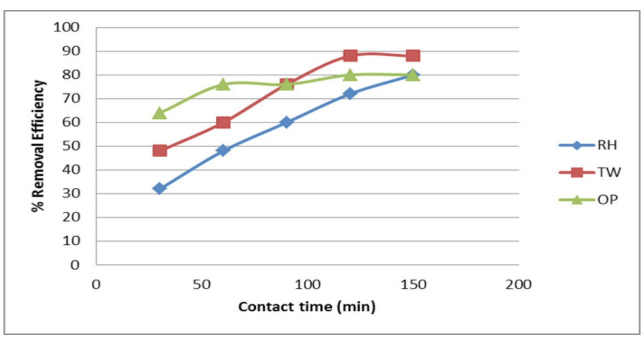

Figure 9. Contact time v/s Efficiency for adsorbents.

3.5 Effect of Initial Metal Ion Concentration

As per Figure 10, with increasing lead concentration, the % removal efficiency for all the adsorbents shows a decreasing effect but the adsorption ability increases. This can be described on the basis that at low concentration, the ratio of lead ions to the number of sites available for adsorption is low; hence the adsorption sites tend to take up available lead ions much quickly due to less competition among lead ions. Also, the adsorbents have a partial number of active sites that get inundated after a certain concentration[5].

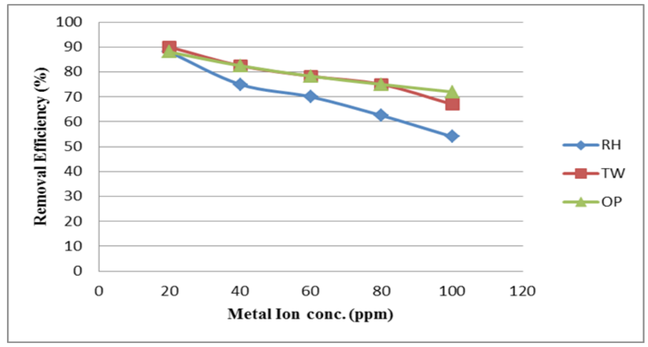

Figure 10. Metal ion conc. v/s Efficiency for adsorbents.

3.6 Adsorption Isotherms

The removal of Pb (II) by the adsorbents has been assessed with respect to Freundlich and Langmuir isotherms of adsorption.

The Langmuir model is based on the theory that on the surface of the adsorbent, only a single layer of the adsorbate is formed. The study of the Langmuir isotherm is important in determining the adsorptive effectiveness of the adsorbent. It is also useful in maintaining the working conditions for successful adsorption[6]. The mathematical relation used for Langmuir isotherm as shown in Figure 11 is

$$\frac{1}{q} = \frac{1}{q_e b}\left(\frac{1}{C}\right) + \left(\frac{1}{q_e}\right) \quad (3)$$

Where, C = concentration of adsorbate (mg/L), q = adsorption capacity (mg/g), q_e = max. adsorption capacity (mg/g), and b = measure of lead ions attraction for adsorbent. The equation gives a correlation between the concentration and the amount of lead ion adsorbed.

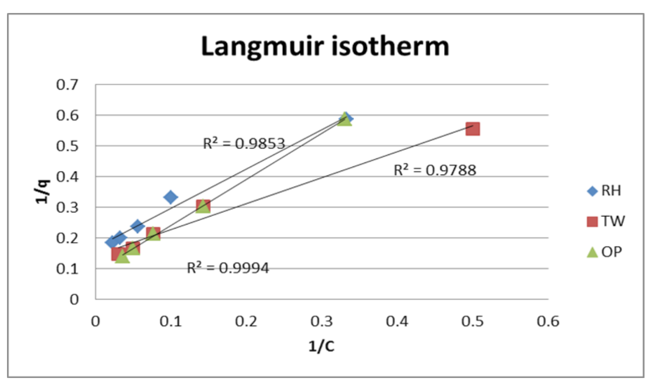

Figure 11. Langmuir isotherm for adsorbents.

Langmuir isotherm is articulated with the help of a constant separation factor, $\mathbf{R_L}$, which indicates the suitability of adsorption, given as:

$R_L = 1/1 + bC_o$

Where $\mathbf{C_o}$ is the initial concentration of lead ion solution (mg/L) and **b** is the adsorption eq. constant (mL/mg). Based on the separation factor effect on the shape of isotherm, the $\mathbf{R_L}$ values lying in the range of $0 < R_L < 1$ indicate the suitability of adsorption[7].

The Freundlich isotherm is obtained from the Langmuir by assuming that there are a number of sites on the adsorbent that have affinity for the adsorbate with each site undergoing monolayer adsorption. The Freundlich isotherm is expressed in terms of an empirical mathematical model where, **C** represents the equilibrium concentration (mg/L), **q** is the amount adsorbed/ amount of adsorbent used at equilibrium (mg/g) and **K** and **n** are constant parameters depending on the adsorbate and adsorbent addressing to adsorption capacity and intensity, respectively[8].

The equation used for the graph in Figure 12 is:

$$\log q = \log K + \frac{1}{n}\log C \quad (4)$$

The equation gives a correlation between the log of concentration and the amount of metal ion adsorbed. The **n** value gives the amount of nonlinearity between the concentration of solution and adsorptive capacity. The values of n>1 show positive and good adsorption.

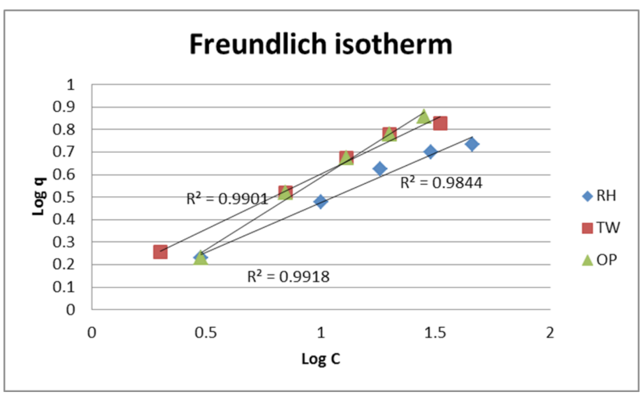

Figure 12. Freundlich isotherm for adsorbents.

The $\mathbf{R_L}$ values are 0.232, 0.192 and 0.401 and **n** values are 2.269, 2.047 and 1.56 for rice husk, spent tea leaves and orange peel respectively. The isotherm studies indicate that the adsorptive behaviour of lead metal ions on adsorbents suits to both the isotherm models.

3.7 Adsorption Kinetics

The kinetics of adsorption is determined by assessing the removal of lead from the solution at various time durations using pseudo-first order and second order equations. The linearity of each plotted model indicates whether the model describes the adsorption process properly or not. The adsorption kinetics is very imperative from the viewpoint of process efficiency[9].

The pseudo-first order equation used is given in Figure 13 as:

$$\log(q_e - q_t) = \log q_e - \frac{k^1}{2.303}t \quad (5)$$

The pseudo second order equation used in Figure 14 is:

$$\frac{t}{q_t} = \frac{1}{k^2 q_e^2} + \frac{t}{q_e} \quad (6)$$

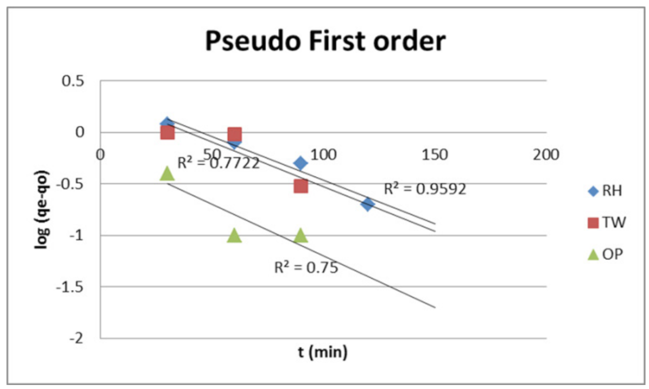

Figure 13. First order kinetics for adsorbents.

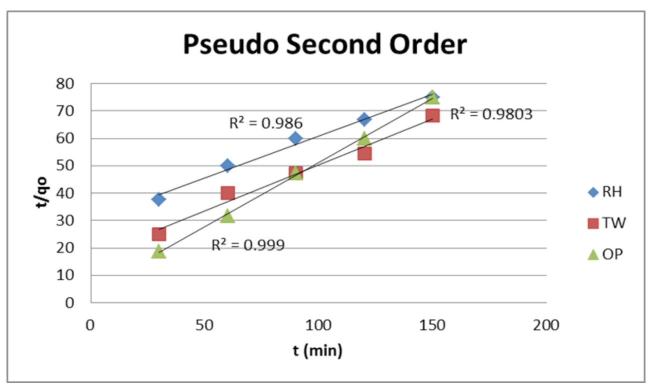

Figure 14. Second order kinetics for adsorbents.

The data is exhibited by using both the kinetic models. According to the results, the pseudo second order kinetics has better linearity in comparison to the first order. The values of q_{eobs} and q_{ecal} for pseudo first order are 2.0 and 2.39 mg/g, 2.2 and 2.21 mg/g, 2 and 1.58 mg/g for rice husk, spent tea leaves and orange peel respectively. The values of q_{eobs} and q_{ecal} for pseudo second order are 2.0 and 3.27 mg/g, 2.2 and 2.972 mg/g, 2.0 and 2.13 mg/g for rice husk, spent tea leaves and orange peel respectively.

4. Conclusions

From the above mentioned study on removing Pb^{2+} ions from artificial solution using rice husk, spent tea leaves and orange peel by batch studies, it may be concluded that

1. All the adsorbents used for the study have a good adsorption potential for Pb (II) from the solution.
2. Batch process has shown that adsorption is greatly reliant on parameters like dose of adsorbent, pH, time of contact and initial concentration of heavy metal ion.
3. The extent of removal of lead by using rice husk has been found to be 80 % for rice husk, 88 % for spent tea leaves and 80 % for orange peel.
4. The optimum pH is found to be 5, 5.5 and 5, optimum contact time is 150 min, 120 min and 120 min and optimum dose is 1g/100 mL for rice husk, spent tea leaves and orange peel respectively.
5. It can be concluded that Tea waste is the most efficient for removing Pb^{2+} from the solution. The ranking order of adsorbents for Pb^{2+} removal is given as: Tea waste > Rice Husk > Orange peel.
6. The data for the lead removal can be explained by using both the isotherms- Langmuir and Freundlich. However, for rice husk and orange peel, Langmuir isotherm showed better correlation and for tea leaves, the results were slightly better for Freundlich isotherm model.
7. Kinetic studies done with the help of the pseudo first order and second order equations show that the surface adsorption contributes to the rate determining step. From the results, it is evident that the adsorption using rice husk shows the best correlation for pseudo first order mechanism whereas, tea leaves and orange peel follow pseudo second order kinetics.
8. Thus, the utilization of agro waste for the treatment of wastewater is one of the likely options which has proved to be efficient, eco-friendly, easily available with no further secondary pollution.

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