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Adsorption of Lead (II) by Naturally Available Waste Material

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Abstract: *The main aim of this work is to determine the adsorptive removal of lead (II) by making use of low cost naturally available biosorbent namely orange peel in original and chemically modified form. The biosorbent were prepared by oven drying orange peel and then chemically modified with sodium hydroxide (0.1M). The adsorption capacities of biosorbent were carried in batch study, using variation of pH, initial lead concentration, contact time, and particle size. The lead (II) concentration was measured by using "HANNA HI 4522" ion analyzer. The equilibrium data for the adsorption of Pb (II) on effective adsorbents was tested with adsorption isotherm models such as Langmuir, Freundlich and Linear. The results indicated that the chemically modified orange peel worked more effectively than original orange peel at equilibrium contact time of 30 min. The effect of particle size on percentage adsorption was marginal for original orange peel. The chemically modified orange peel showed effective at 75*µ particle size. *The Langmuir isotherm model was found to be the most suitable one for chemically modified orange peel (75µ). The kinetic study was carried out only for chemically modified orange peel and it was found to follow a pseudo second-order rate equation.*
Keywords – *Adsorption, Biosorbent, Isotherm model, Lead (II), Orange Peel*

I. Introduction

The presence of toxic heavy metal contaminants in wastewater streams and industrial effluents is one of the most important environmental issues being faced world over. Lead (II) is a priority pollutant which is highly toxic, carcinogenic and non-biodegradable metal. It directly enters the water bodies through the effluent discharges coming from battery, paper and pulp, mining, electroplating, lead smelting and metallurgical finishing industries [1]. It has harmful effects on human, plants as well as soil [2]. In order to get rid of this problem commonly used techniques are chemical precipitation, ion exchange, reverse osmosis, solvent extraction and membrane process [3]. However, these techniques have certain disadvantages such as incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge [4].The removal of toxic heavy metal at very low concentrations from water can be accomplished by adsorption method [5].

At present, economic crises strongly recommended the use of 'low cost adsorbent', due to their local availability, technical feasibility, engineering applicability and cost effectiveness. [6]. Low cost adsorbent includes materials originated from agricultural sources and by-products (fruits, vegetables, and foods), agricultural residues and wastes. [7].

In the present study, two biosorbent original and chemically modified prepared from orange peels were used. The main objective of this comparative study was to investigate the feasibility of original and chemically modified peels at different particle size (300µ and 75µ).

II. Materials and Methods

2.1 Chemicals

All chemicals used in this study were pure analytical grade. Stock solution (1000 mg/L) of heavy metal was prepared by dissolving Pb $(NO_3)_2$ in de-ionized water and then diluted to desired concentrations. 0.1M NaOH was used for modification of orange peels.

2.2 Preparation of biosorbent

Orange peel was selected because it was generated in large quantities as solid waste from local fruit juice centre.

2.2.1 Original peel (OP)

Original orange peels were cut into small pieces and washed with de-ionized water and dried in the oven at 60^oC for 24 hrs until reached a constant weight. Dried peels were ground and sieved through 425µ, 300µ and 75µ sieve. For preservation, it kept in plastic-stopper bottles.

2.2.2 Chemical modification of original peel

Modification was carried out by soaking dried original orange peels in 0.1M NaOH (10g of peel/100ml) for 24 hrs, rinsing with de-ionized water, and dried in oven at 60^oC for further 24hrs until reach a constant weight. Dried peels were ground and sieved through 425µ, 300µ and 75µ sieve. For preservation, they are kept in plastic-stopper bottles. [6].

2.3 Experimental procedure

2.3.1 Batch adsorption studies

The batch studies were performed on original orange peel and chemically modified with (0.1M NaOH) to find out effective materials. Each batch adsorption experiments were performed to determine the effect of various parameters (metal concentration, particle size and contact time) on the sorption of lead (II) onto the peels, at constant room temperature.

Accurately weighed amounts of biosorbent (0.1g) were added to conical flasks containing 100ml of metal solution at a various concentration (50, 100, 150 and 200 ppm). The 1:1000, solid to liquid ratio was maintained throughout the study. The mixtures were stirred using a shaking thermostat machine at a speed of 120 r/min. Samples were filtered through Whatman filter paper (No.42) and the filtrates were analyzed for residual metal ion concentration by "HANNA HI 4522" ion analyzer.

Where, Co and C_{eq} are the initial and equilibrium concentration of lead in the effluent (mg/l). V is the volume of waste solution (ml) and M is weight bio-sorbent used (g).

2.3.2 Preliminary experiments

In order to study the dependence of Pb (II) sorption on particle size, experiments were carried out with different particle size fraction (passing through 425µ and retained on 300µ, 75µ). A 0.1 g of biomass was added to conical flasks containing100 ml of metal solution (50,100,150 and 200 ppm). The mixture was stirred magnetically at equilibrium contact time for various biomasses, at room temperature and at pH 5.

The effect of contact time on sorption of lead (II) was obtained by agitating 100 ml of metal solution (50,100,150 and 200 ppm) with contact time of 1/2hr, 1hr, 4hr, 8hr, at room temperature

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2.3.3 Sorption Kinetics

The kinetic studies were carried out by performing the batch sorption experiments with initial metal concentrations of 50 to 200 ppm at different time periods varying between 30 min and 480 min. [6]. Both pseudo-first- and second-order kinetic models were used to analyze the kinetics of the sorption process. [8].

2.3.4 Sorption isotherm

Adsorption isotherms were measured by varying the initial metal ion concentrations at constant adsorbent dosage. Experimental data were compared using different sorption models such as Langmuir, Freundlich and Linear.

III. Result and Discussion

3.1 % Removal efficiency of lead (II) using original and chemically modified orange peel

Lead (II) adsorption was determined as a function of time to determine an optimum contact time for the adsorption of Pb (II) ions on original and chemically modified orange peel. From Fig.1 , the 80% removal of metal ion were take place within 30 minutes of contact time at 50ppm concentration using original orange peel. No significant variation in percentage removal of metal ion was observed by increasing contact time. In the initial stages of adsorption of Pb^{2+}, the concentration gradient between the film and the available pore sites was large, and hence the rate of adsorption of Pb^{2+} was faster [9].Chemically modified orange peel showed that the surface modifications gave significant effect on the surface area of the original peel.

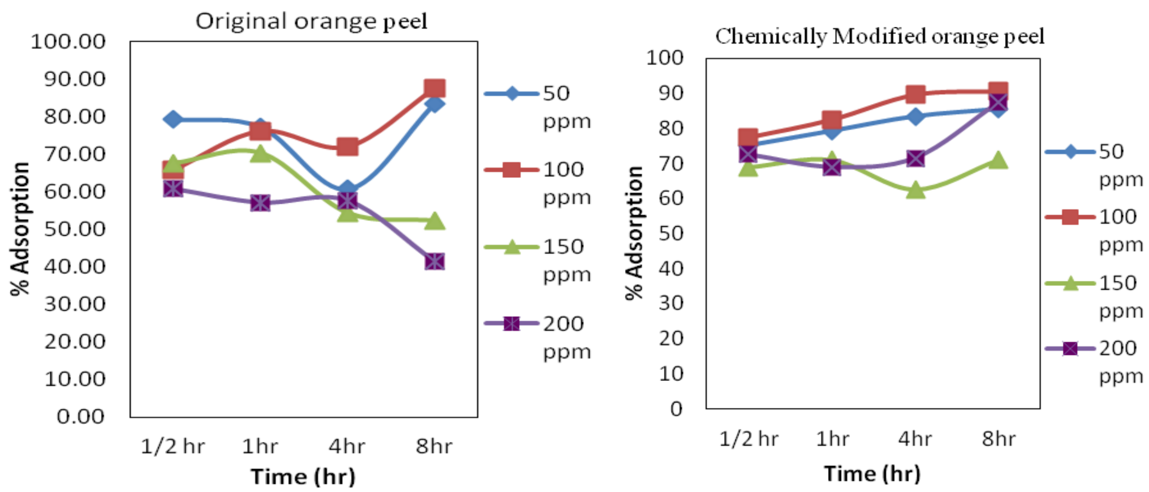

Fig. 1 % Removal efficiency of lead (II) using original and chemically modified orange peel

3.2 Effect of particle size on removal efficiency of lead (II) using original and chemically modified orange peel

The percentage removal of lead concentration w.r.to particle size and contact time between original and alkali modified peels as shown in Fig.2. There was an increase in percentage removal of lead with chemically modified peel compared to original peel.

The chemically modifying of the biosorbent increases the number of carboxylate ligands, which can enhance the binding ability of the biosorbent. The effect of particle size on adsorption was predominantly observed at higher lead concentration. Thus it can be concluded that at 75µ particle size, the marginal increase in percentage removal of lead at lower concentration was due to increase surface area.

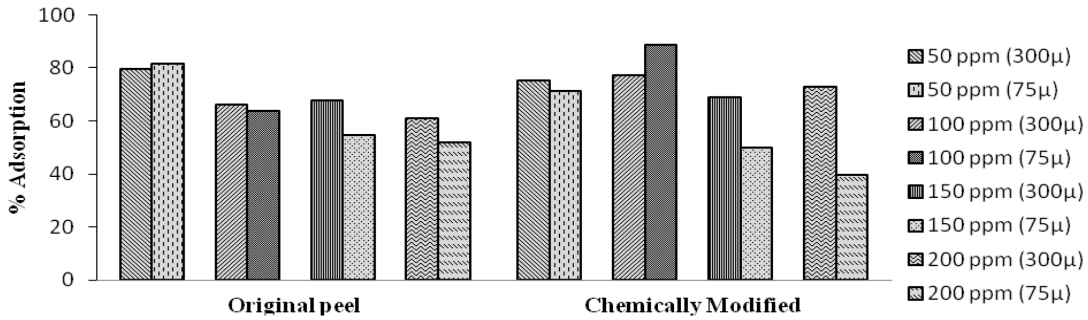

Fig. 2 Effect of particle size on removal efficiency of lead (II) using original and chemically modified orange peel

3.3 Adsorption Isotherms

Linear, Langmuir and Freundlich models are used to describe adsorption isotherms. Based on the assumption that all adsorption sites are equivalent and adsorption in active sites is independent of whether the adjacent is occupied, the Langmuir adsorption model can be expressed as [8].

$$\frac{C_e}{C_s} = \frac{1}{K_1 . b} + \frac{C_e}{b} \qquad (1)$$

Where, C_e is the equilibrium concentration of adsorbate (mg/l), C_S is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). K_l is Langmuir isotherm constant (L/mg), also b is maximum monolayer coverage capacity (mg/g). According to this equation, the plot C_e versus C_e / C_s should be straight line with slope 1/b and intercept $1/K_1 b$.

Similarly, the Freundlich equations can be expressed as

$$\log C_s = \log (K) + n^{-1} \times \log C_e \qquad (2)$$

Where, K and n are Freuendlich isotherm constant and adsorption intensity. The plot of log C_e versus log C_s should be straight line with slope 1/n and intercept K.

The effect of initial metal ion concentration, chemical modification, also particle size on Pb^{2+} removal was investigated and observed that chemically modified (75µ) orange peel works effectively as compared to original at equilibrium contact to time. So isotherm models were discussed below for chemically modified peel.

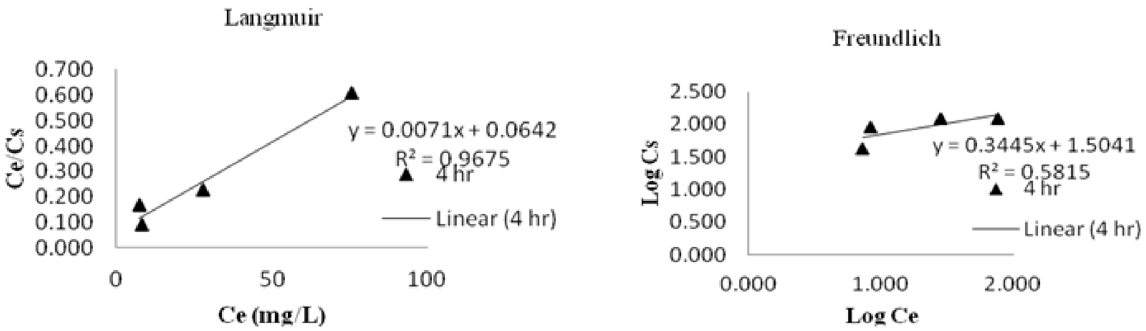

Fig. 3 Langmuir and Freundlich isotherm model of lead (II) ions onto chemically modified orange peel

From Fig.3 and Table 1, the regression (R^2=0.966) value obtained from the Langmuir isotherm was found to be higher than Freundlich isotherm. The Langmuir constant b was obtained as 1.42 mg/g. The Langmuir constant K_1, which denotes adsorption energy, was found to be 0.109 L/mg. So Langmuir isotherm was best fit for chemically modified orange peel (75µ).

Table 1 Calculated isotherm constants for the adsorption of lead (II) using chemically modified orange peel

Chemically Modified (75µ)	Langmuir			Freuendlich		
	K_1 (l/mg)	b(mg/g) X 100	R^2	K	1/n	R^2
Orange	0.109	1.42	0.967	31.915	0.344	0.581

3.4 Adsorption Kinetics

The controlling mechanism or rate determining step of lead (II) uptake on the banana peel was studied by Lagergern pseudo first order and second order models [10]. It was conclude that chemically modified orange peel (75µ) works effectively as compared to original peel. So adsorption kinetic studies were discussed for chemically modified peel.

Pseudo-first-order kinetic model known as the Lagergern equation can be expressed as [11]

$$\log (C_S - C_t) = \log C_S - \left(\frac{K_1 t}{2.303}\right) \qquad (3)$$

Where, C_s and C_t are the amounts of lead (II) adsorbed (mg/g) at equilibrium time and at any instant of time, t, respectively, and K_1 (L min^{-1}) is the rate constant of the pseudo first- order adsorption operation. The plot of log ($C_S - C_t$) verses t gives a straight line for the pseudo first-order adsorption kinetics, from the adsorption rate constant, K1, is estimated.

Pseudo- second -order kinetic model known as the Lagergern equation can be expressed as [12]

$$\frac{t}{Cs} = \frac{1}{h} + \left(\frac{1}{Cs}\right) t \qquad (4)$$

Where, K_2 (gm g^{-1} min^{-1}) is the second order rate constant. h= K_2 C_s^2 that can be regarded as the initial adsorption rate as $t \rightarrow 0$. Under such circumstances, the plot of t/C_s versus t should give a linear relationship, which allows the computation of C_s and K_2.

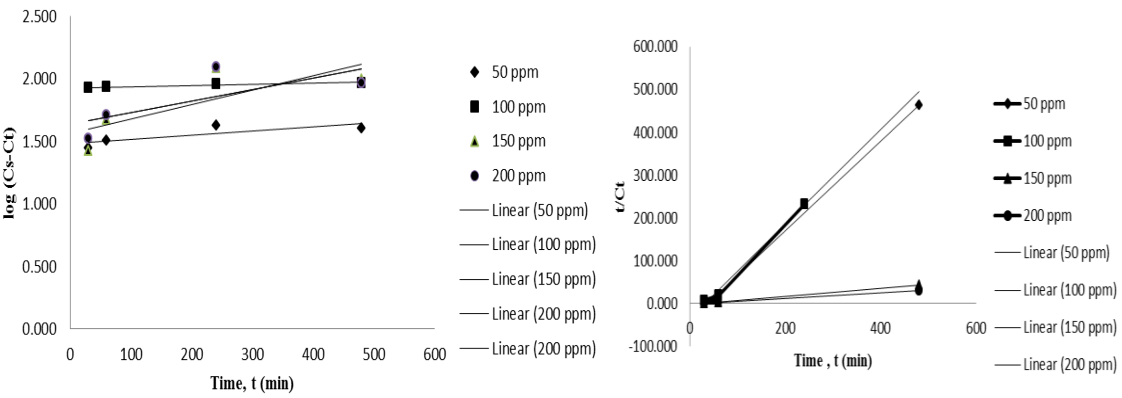

Fig. 4 Pseudo- first & second order adsorption kinetic plots for chemically modified orange peel

Table 2 Calculated kinetic parameters for chemically modified orange peel

C_o	R^2	
	Pseudo first Order equation	Pseudo second Order equation
50ppm	0.647	0.997
100ppm	0.901	0.992
150ppm	0.613	0.998
200ppm	0.55	0.999

Fig.4 and Table 2 shows that , on comparing the correlation coefficient $R^2$of pseudo first order and second order kinetic model, the second order showed the higher value hence the adsorption follows pseudo second order kinetics for chemically modified orange peel (75µ).

IV. Conclusions

The adsorption capabilities of original and chemically modified orange peel for removing lead (II) from aqueous solution was studied in the present work. Batch experimental studies showed that lead (II) could be effectively removed by chemically modified orange peel. At lower lead concentration (50 ppm), chemically modified orange peel worked effectively and maximum removal efficiency was achieved within 30min of contact time. The effect of particle size (300µ and 75µ) was marginal. The isotherm equilibrium study was carried out for chemically modified orange peel (75µ) at equilibrium contact time and it suggested that the Langmuir isotherm model was found to be best fitting. Kinetic studies suggested that lead adsorption on modified orange peel adsorbent could be followed more favorably by the pseudo-second-order kinetic model.

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