

Removal of Pb (II) ions from Aqueous Solution using Natural Orange Peel and Activated Orange Peel

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Abstract - The objective of this paper was to study the removal of lead ions by adsorption using cheap and eco-friendly natural & activated orange peel adsorbent from aqueous solution. The lead Pb (II) ions removal from aqueous solution was studied using batch adsorption method. The main parameters that influenced lead adsorption were contact time, adsorbent dosage and pH value. Characterization of natural orange peel (NOP) and activated orange peel (AOP) has been studied by SEM, TEM and FTIR. Equilibrium data showed that lead adsorption fitted well with adsorption isotherm models. The maximum removal of lead by natural orange peel and activated orange peel is 79% and 98% respectively.

Keywords: Lead, Natural orange peel, Activated orange peel, Adsorption Isotherms.

1. INTRODUCTION

Lead (Pb II) ions is a heavy metal that is released in natural water from glass industries, ceramic, textile dyeing, petroleum refining, battery manufacturing and mining operations. It contaminate drinking water due to the corrosion, leaching of lead from water pipes and lead solder joints associated in service lines used in household plumbing. It is highly and cumulative poison accumulates mainly in bones, kidney, brain & muscles. International Agency for Research on Cancer categorised lead as probably carcinogenic to humans. It is also an oxidising agent. It must be handled and stored with the appropriate safety and precautions to prevent inhalation, skin contact and ingestion [1]. Manufacturing industries such as batteries, television tube, paints, pigments, photographic material, printing, gasoline additives, matches and explosives brought lead bearing wastewater [2]. Industrial effluents must be free from lead before its discharge to prevent environmental hazard [3]. Due to its hazardous nature, "In this study an attempt was made using adsorption technology for the removal and minimization of toxicity of Pb (II) ions by natural and activated orange peel, using batch studies and isotherm studies for determination of adsorption capacities" [4-5].

2. MATERIALS AND METHODS

2.1. Chemicals

Lead nitrate ($Pb(NO_3)_2$), sulphuric acid (H_2SO_4), Hydrochloric acid (HCl) and also distilled water was used in this experiment. All chemicals were analytical reagent grade.

2.2. Adsorbents used

2.2.1. Natural orange peel powder

Oranges as a fruit are produced in large amount in India and their peels are treated as waste materials. Thus they are available very easily and free of cost in abundant. First washing of orange peels were done with distilled water to remove dirt and unwanted particles from it. Then they were cut into small pieces and kept into oven at $90^{\circ}C$ for 15-20 hrs. Then after drying they were crushed in a grinder and then they converts into fine powder. The powder was sieved.

2.2.2. Activated orange peel

Sulphuric acid is added in orange peel powder formed by above procedure and heated in furnace at temperature $150-155^{\circ}C$ for 20 min. Then it converts into carbon & this carbon was cooled at room temperature. Washed with distilled water to remove acid from it and dry it in oven to remove moisture from it.

2.3. Adsorbate

Stock solution of 1000 ppm of Pb (II) ions was prepared by adding 1.6 g of lead nitrate in 1000 ml distilled water in 1000 ml flask.

2.4. Batch adsorption studies

Batch technique was used to study adsorption of Pb (II) ions. 0.5 g of adsorbent was taken with 50 ml of Pb (II) ions solution of concentrations 20, 40, 60, 80, 100 ppm in beakers at room temperature on

shaker for a known period 90-120 min. The suspension of adsorbent was separated from the solution by filter paper. The concentration of lead ions remaining in the solution was measured by UV-Vis spectrophotometer. The effect of several parameters, such as pH, concentrations, contact time and adsorbent dose for the adsorption were studied and the pH of the adsorptive solutions was adjusted using HCl, buffer solutions and NaOH [6]. The obtained results of these studies were used to calculate the optimum conditions for maximum heavy metals removal from aqueous solution [7]. The removal of Pb (II) ions was calculated by given equation (1)

$$\text{Dye removal efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

2.5. Characterization Techniques

SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid objects. It reveals information of external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. TEM is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image [8]. FTIR is used to identify certain functional groups in molecules [9].

2.6. Adsorption isotherm

Langmuir isotherm was observed the equilibrium relation between amount of adsorbate adsorbed on the adsorbent surface and its concentration in the solution at constant temperature. The linear form of Langmuir expression is given by (2)

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_0} + \frac{1}{(b Q_0)} \quad (2)$$

Where C_e is the equilibrium concentration of dye solution (mg/l), Q_e is the equilibrium capacity of Pb (II) ions on the adsorbent in mg/g, Q_0 is the monolayer adsorption capacity of the adsorbent and b is the constant and is related to the free energy of adsorption.

$$Q_e = (C_0 - C_e) \frac{V}{W} \quad (3)$$

Q_e = adsorption capacity, C_0 =initial concentration,

C_e = equilibrium concentration, V = volume of solution, W =amount of adsorbent

Freundlich isotherm shows that several layers of adsorbate formed on the surface of adsorbent. This model is based on the assumptions that lead ions are adsorbed on a heterogeneous surface and is not restricted to formation of monomolecular layer. The linear form can be written as equation (4)

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

K_f and $1/n$ are the constants which indicate the adsorption capacity (mg/g) and intensity of the adsorption.

3. RESULT AND DISCUSSIONS

3.1. Characterization

SEM routinely used to generate high-resolution images of shapes of specimens and to show spatial variations in chemical compositions of AOP and NOP. Fig. 1 and 2 shows NOP and AOP image, we can see the irregular shapes. A porosity and uniform surface can be seen in both the figures. In these images, the presence of many pores proves the important role of ultrasonic waves on carbon activation. TEM was used to determine the size and size distribution of the NOP and AOP. The size of NOP and AOP was 2 μm and 100 nm respectively with non uniform shape. FTIR spectrometer shows high spectral resolution data over a wide spectral range of a solid, liquid or gas. The broad and intense peaks at 3762 cm^{-1} and this FTIR spectra showed that the peaks expected at 3762, 3017, 1810, 1502, 1283 and 821 cm^{-1} had shifted to 3723, 3004, 1808, 1489, 1271 and 795 cm^{-1} due to adsorption [10-11]. The shift may be due to changes in counter ions associated with carboxylate and hydroxylate anions.

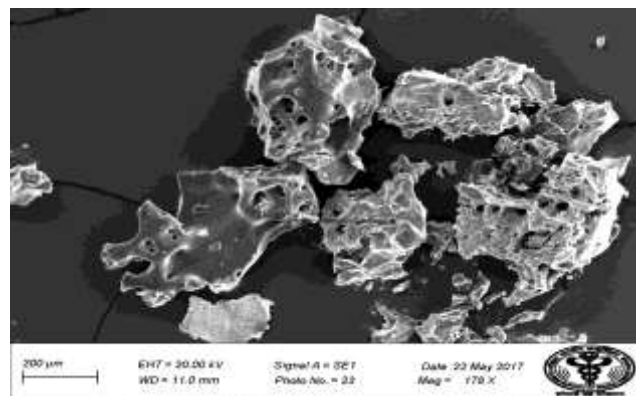


Fig. 1. SEM image of Natural orange peel

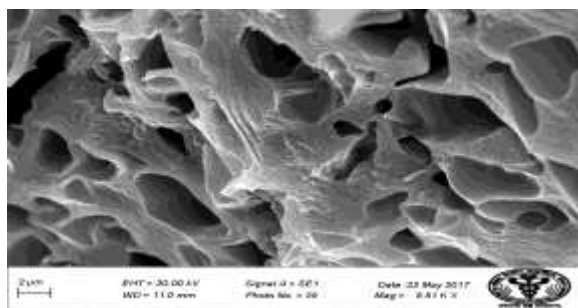


Fig. 2. SEM image of activated orange peel

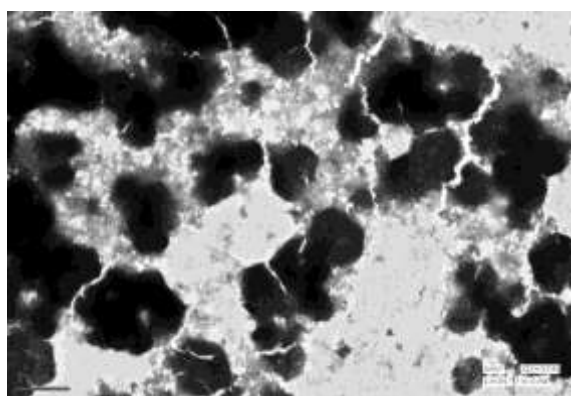


Fig. 3. TEM image of natural orange peel

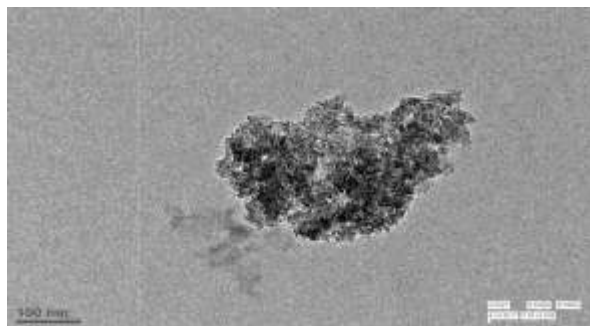


Fig. 4. TEM image of activated orange peel

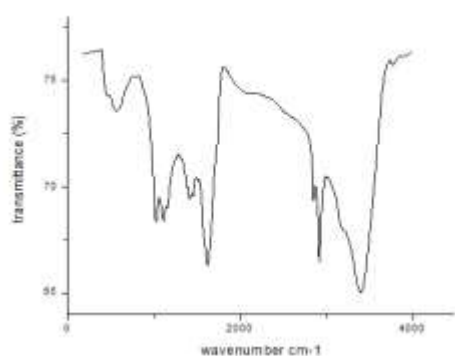


Fig. 5. FTIR of natural orange peel

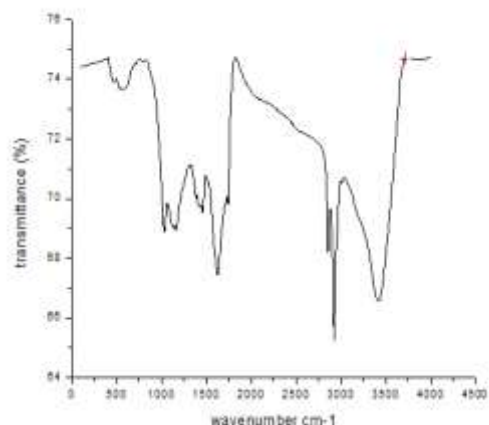


Fig. 6. FTIR of activated orange peel

3.2. Adsorption Studies

3.2.1. Effect of contact time variation

Fig. 7 shows the effect of contact time using both cases natural orange peel and activated orange peel for adsorption of Pb (II) ions of 20 ppm concentration. 0.5 g adsorbent (AOP & NOP) was taken in 100 ml beaker and total 50ml solution was prepared of Pb (II) ions. Thus beaker of sample was kept on the shaker at room temp 30⁰C. The contact time for sample was taken as 20, 30, 40, 50, 60, 70, 80 min etc. The % of absorbance at 283 nm was determined by UV-spectrophotometer. Adsorption increases with increase in contact time and it becomes constant after 60 minutes [12]. Maximum removal efficiency was 94.56 % in case of AOP and 74.55 % in case of NOP.

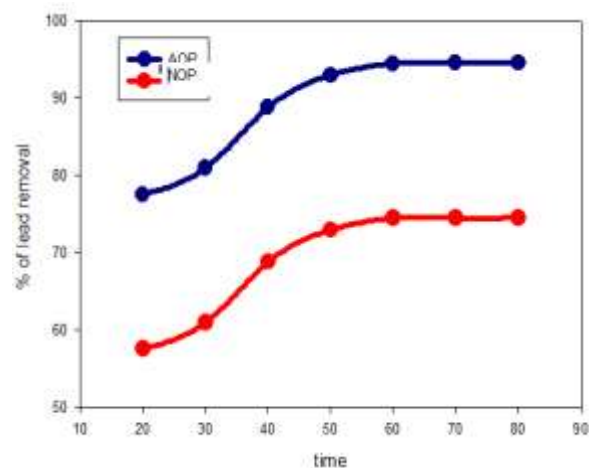


Fig. 7. Effect of contact time on % removal of Pb (II) ions by AOP & NOP at adsorbent dose 0.5 g, pH 6

3.2.2. Effect of adsorbate dosage variation

Fig. 8 shows that the effect of dose of adsorbent was studied in both cases. Pb (II) ions concentration was kept 20 ppm, adsorbent dose 0.5g, total volume of solution 50ml was taken. Different concentration of adsorbent was taken in 4 different beakers of 0.2, 0.4, 0.6, 0.8 g respectively. Samples were kept for 120 min on the shaker at room temperature, % absorbance at determined. It was observed that % removal of Pb (II) ions increases with increase in adsorbent dosage [13]. Maximum Pb (II) ions removal in case of AOP was 95.43% and maximum lead removal in case of NOP was 75.34%.

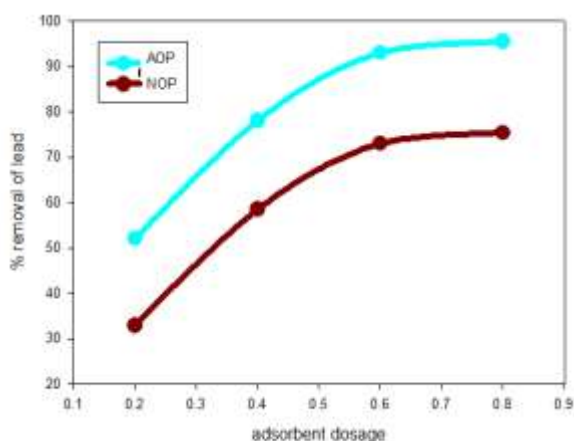


Fig. 8. Effect of adsorbent dose on removal of Pb (II) ions by AOP and NOP

3.2.3. Effect of pH variation

Fig. 9 shows that the effect of pH and Pb (II) ions of concentration 20 ppm was taken but their pH was different 2, 4, 6, 8, 10. Adsorbent amount was 0.5 g and total volume of the 5 samples was taken 50ml. These samples were kept on the shaker for 120 min at room temperature. It was observed that percentage removal of Pb (II) ions increases with increase up to pH 6. Then there is decrease in percentage removal of Pb (II) ions with increases in pH [14]. Thus maximum removal of Pb (II) ions 98.37% for AOP and maximum removal of Pb (II) ions 78.73% for NOP.

3.2.4. Effect of initial concentration

Fig. 10 shows that the effect of concentration was studied that in the both cases (AOP & NOP) total 50 ml solution of lead was taken at different concentration 20, 40, 60, 80, 100 ppm in 5 different beakers. They kept on the shaker for 120 min at room temperature. The samples were shaken at pH 5.6. It was observed that maximum % removal occurred at very low concentration thus % removal of

Pb (II) ions decreases with increase in concentration. Maximum and minimum removal of Pb (II) ions at 20 ppm and 100 ppm was 93% and 69.59% respectively for AOP. For NOP maximum and minimum removal was 73% and 49.29%.

3.2.5. Study of temperature

The influence of solution temperature on Pb (II) ions removal is depicted in Fig. 11. The experimental data obviously showed that by increasing the solution temperature from 30 to 60 °C. The 0.5 g adsorbent added and then kept for shaking by magnetic beats for 120 min. Removal of Pb (II) ions increases with increase in temperature and maximum removal of Pb (II) ions was 94.63% for AOP and 78% for NOP. Temperature increase leads to increase in number of adsorption sites due to breaking of some internal bonds near edge of active surface sites of adsorbent [15].

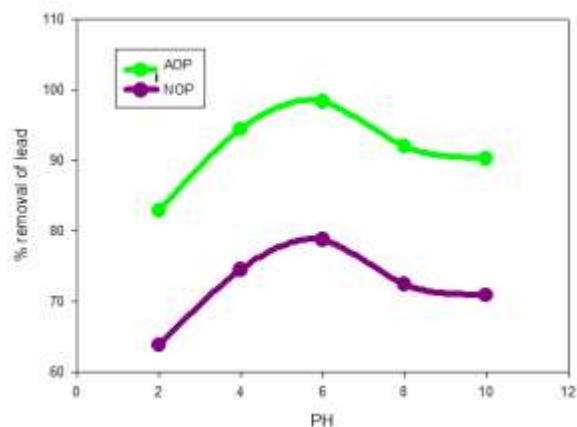


Fig. 9. Effect of pH on removal of Pb (II) ions by AOP & NOP

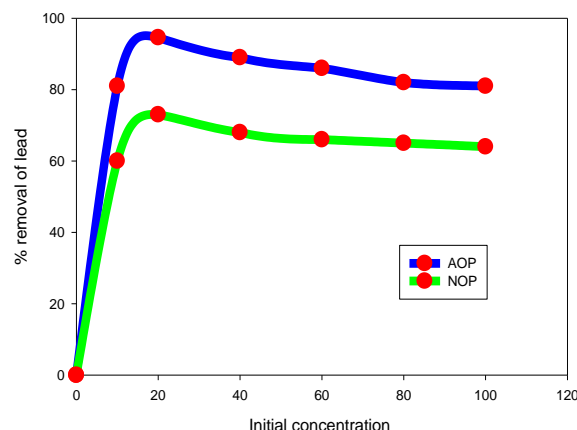


Fig. 10. Effect of initial concentration on % removal of Pb (II) ions by AOP & NOP

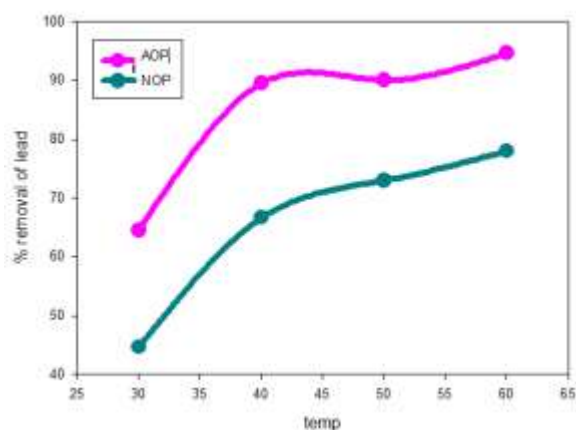


Fig. 11. Effect of temp on % removal of Pb (II) ions by AOP & NOP

3.3. Adsorption isotherms

Langmuir model was fitted to the experimental data as shown in fig. 12 and 13 for NOP and AOP respectively.

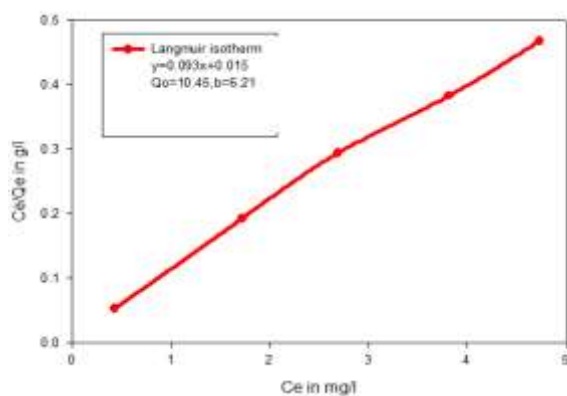


Fig. 12. Langmuir isotherm for AOP

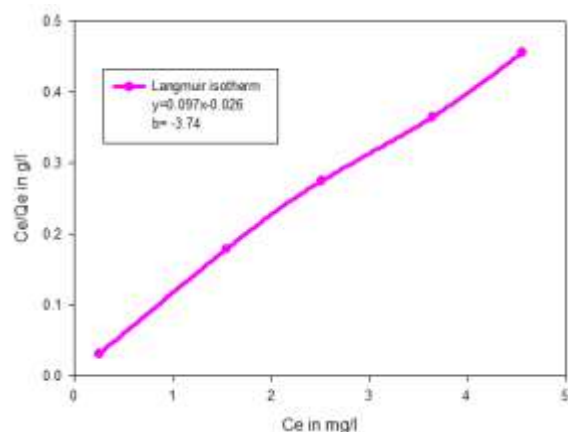


Fig. 13. Langmuir isotherm for NOP

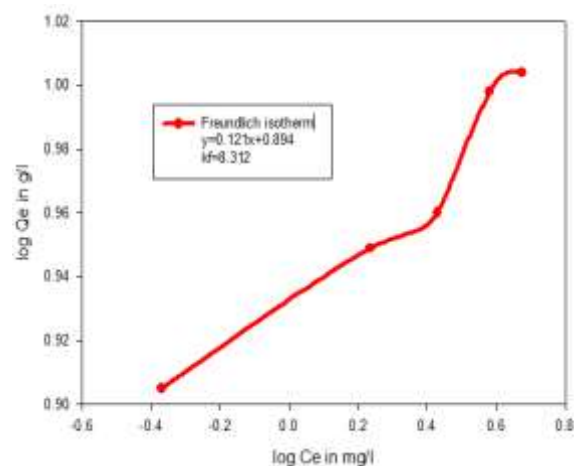


Fig. 14. Freundlich isotherm for AOP

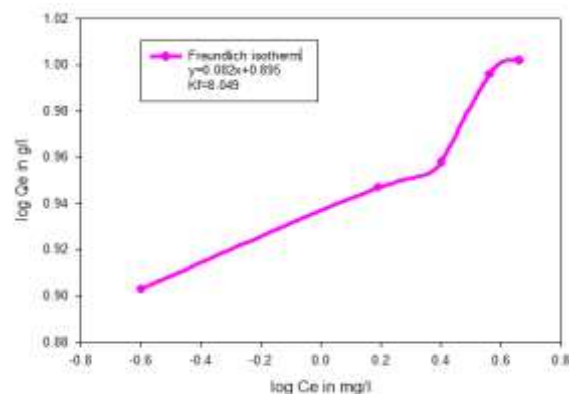


Fig. 15. Freundlich isotherm for NOP

The R^2 value is close to 1 and thus both the models describe the system but Langmuir isotherm model fits better than Freundlich isotherm model.

Table.1. Evaluated adsorption constants for AOP and NOP at room temperature observed for different Isotherm models

	Langmuir Isotherm model			Freundlich Isotherm model		
	Q_0	K_L	R^2	N	K_f	R^2
AOP	0.093	6.21	0.989	0.121	8.312	0.937
NOP	0.097	3.74	0.978	0.082	8.049	0.912

3.4 Dynamic modeling

The kinetics of adsorption is important from the point of view that it controls the process efficiency. Various kinetic models have been used by various researchers and different systems conform to different models but the Lagergren's rate equation (Lagergren 1898), is the one most widely used [17] for the sorption of a solute from a liquid solution. Thus the first-order equation written as equation (5)

$$\log (q_e - q) = \log q_e - (K_{ads} / 2.303) t$$

where q_e and q are amount of lead adsorbed at equilibrium and at time t , in mg/g respectively, and K_{ads} is the first order rate constant, was applied to the present studies of dye adsorption. As such, the values of $\log (q_e - q)$ were calculated from the kinetic data of Fig. 7 and plotted against time. The plots so obtained are found to be linear with good correlation coefficients of 0.9242 and 0.9748 for AOP and NOP indicating that Lagergren's equation is applicable to the Pb (II) ions adsorption on AOP and NOP respectively. So this adsorption is a first-order process. The first-order rate constant calculated from the plots is found to be $2.717 \times 10^{-4} \text{ min}^{-1}$ and $0.6 \times 10^{-4} \text{ min}^{-1}$ for AOP and NOP respectively.

4. CONCLUSION

The result has shown that both natural orange peel and activated orange peel were very effective adsorbents for the removal of Pb (II) ions from waste water solutions. The maximum removal of lead by NOP & AOP at pH 6, contact time 80 min, concentration 20 ppm and 1.0g/100 ml adsorbent dose is 79% and 98% respectively.

5. ACKNOWLEDGEMENT

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