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Sorption of Lead (II) Ions from Aqueous Solution by Acid Modified and Unmodified Papaya Seed

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ABSTRACT

The removal of Pb (II) ion from aqueous solutions onto chemically modified papaya seed was studied at varying initial metal ion concentrations, adsorbent doses, pH and contact time. Batch experiments were carried out to evaluate the adsorption capacity of the papaya seed chemically modified with citric acid. The residual Pb (II) ion concentrations after biosorption were analyzed by UV- Visible and FTIR spectroscopy. The characterization of the papaya seed biomass suggested the possible contribution of carboxyl and hydroxyl groups in Pb(II) biosorption. The biosorption efficiency of the papaya seed was examined under various factors like pH, contact time and adsorbent dose. The adsorption data was verified using Langmuir and Freundlich isotherm model. The present study revealed that citric acid modified papaya seed could be used as an efficient sorbent for the removal of Pb(II) ion from aqueous solutions.

Keywords: Adsorption isotherms, Pb (II) ions, papaya seed, biosorption.

INTRODUCTION

Biosorption is a process that utilizes inexpensive biomass to sequester toxic heavy metals and is particularly useful for the removal of trace level of contaminants from industrial effluents. Compared with conventional methods, such as chemical oxidation and reduction, precipitation and membrane separation, bio sorption process has several advantages, including low operating cost, minimization of the volume of chemical and biological sludge to be disposed of, high efficiency in detoxifying extremely dilute effluents, and no nutrient requirements [1]. Agricultural by-products have been widely studied for metal removal from waste water. These include peat, wood, pine bark, banana pith, soybean and cotton seed hulls, rice husk, saw dust, tamarind seeds, compost and leaves [2].However, the untreated plant waste which are used as bio adsorbent have lower adsorption capacity, higher Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) as well as Total Organic Carbon (TOC), it is due to the release of soluble organic compound present in the plant material [3].Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters [4].As these heavy metals in wastewater are not biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which leads to several health problems in animals, plants and human beings. As a result of the degree of the problems caused by heavy metals pollution, hence removal of heavy metals from wastewater is important[5].Papaya seed is composed of lignin and cellulose as major constituents and may also contain other polar functional groups of lignin, which include alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. These groups have ability to some extent to bind heavy metal ions by donation of an electron pair from these groups to form complexes with the metal ions in solution [6].

MATERIALS AND METHODS

Preparation of adsorbent: The papaya fruits were popular for their medicinal values. Papaya seeds were collected from the local market fruit stall of Allahabad. The seeds of the fruit were collected in pearl pet container, and brought to the chemistry laboratory then cleaned thoroughly with distilled water and soaked for 24 h in distilled water. The soaked seeds were dried in the shade in the laboratory and powdered by laboratory grinder. The sample was divided into two parts, one part for modified, using citric acid and other part for unmodified. The modification process was done by adding 30cm^3 of 0.5 mg L^{-1} solution of citric acid into the sample and was stirred until the acid mixed properly with the sample to form slurry, it was then kept for an hour and then dried in the oven at 60^{0}C FT-IR spectroscopy was used to identify the functional groups present in the modified and unmodified papaya seed. FT-IR spectra of the modified and unmodified papaya seed were recorded in the range 4000-400 cm^{-1} using a, Digilab Merlin 2000 model FT-IR spectrometer with KBr discs.

Preparation of adsorbate solution Lead (II) solution: The 30 ppm aqueous solution of lead was prepared from $Pb(NO_3)_2$ salts by dissolving 0.025 g salt in distilled water. Other concentrations (10 and 20 ppm) were obtained from this stock solution by serial dilution.

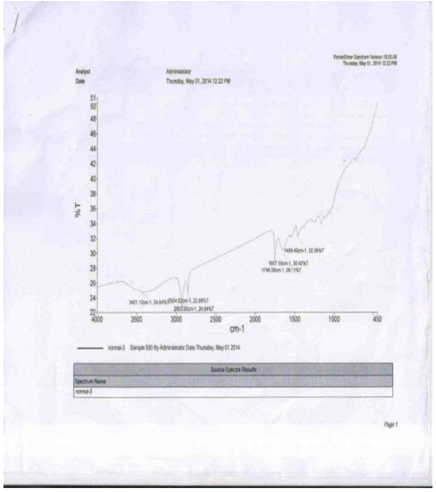
Single batch sorption experiment: All batch biosorption experiments were carried out in 125 mL glass stoppered Erlenmeyer flasks containing 100 mL of aqueous Pb (II) solution with 0.125 g of bio- sorbent. The flasks were agitated at a constant speed of 180 rpm for 1 h in an incubator shaker. The pH values of the solution were adjusted with dilute 0.1 N HCl or 0.1 NaOH. The time required for reaching the equilibrium was estimated by drawing samples at regular time intervals. The bio sorbent was separated by filtration and the metal content in the filtrate was determined by UV-Visible spectrophotometer (Globe instrument microprocessor). The values of percent metal uptake by the sorbent (Sorption efficiency) and the amount of metal ion adsorbed has been calculated using the following relationships.

$$\text{Sorption efficiency} = (C_i - C_f / C_i) \times 100$$
$$\text{Amount adsorbed } (qe) = (C_i - C_f / m) \times v$$

Where,
C_i = initial concentration of metal ion in the solution (mg L^{-1})
C_f = final concentration of metal ion in the solution (mg L^{-1})
m = mass of adsorbent (g L^{-1})
v = volume of solution (L)
qe = amount of metal ion adsorbed per gram of adsorbent

RESULTS AND DISCUSSION

Characterization of the adsorbent: The broad and intense absorption peaks in modified and unmodified papaya seed at 3300-3500 cm^{-1}correspond to O-H stretching vibrations of cellulose, pectin, absorbed water, hemicellulose and lignin. The peaks at 2924 cm^{-1} can be attributed to C-H stretching vibrations of methyl, methylene and methoxy groups. The peaks at 2851- 2855 cm^{-1} can be assigned to the stretching of OH groups bound to the methyl group (C-OH). The presence of the peaks at 1746 cm^{-1} attributed to the carbonyl group (C=O) of carboxylic acid or ester and peaks at 1657 cm^{-1} can be attributed to the −C=O stretching of carboxylic acid with intermolecular hydrogen bond. The adsorption peak at 1460 cm^{-1} could be attributed to the −C−O group. Presence of extra peaks in modified papaya seed at 1235 cm^{-1} is due to the ester group. The cellulose and lignin can react with citric acid during modification **[7].**The cellulosic hydroxyl groups combined with citric acid anhydride to form an ester linkage and introduced carboxyl groups to the papaya seed.



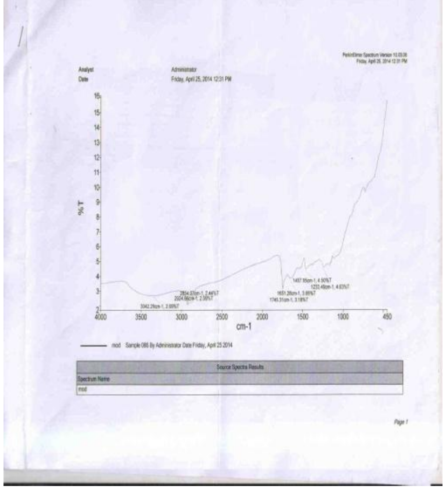


Fig.1: FTIR spectra of unmodified papaya seed **Fig.2:** FTIR spectra of modified papaya seed

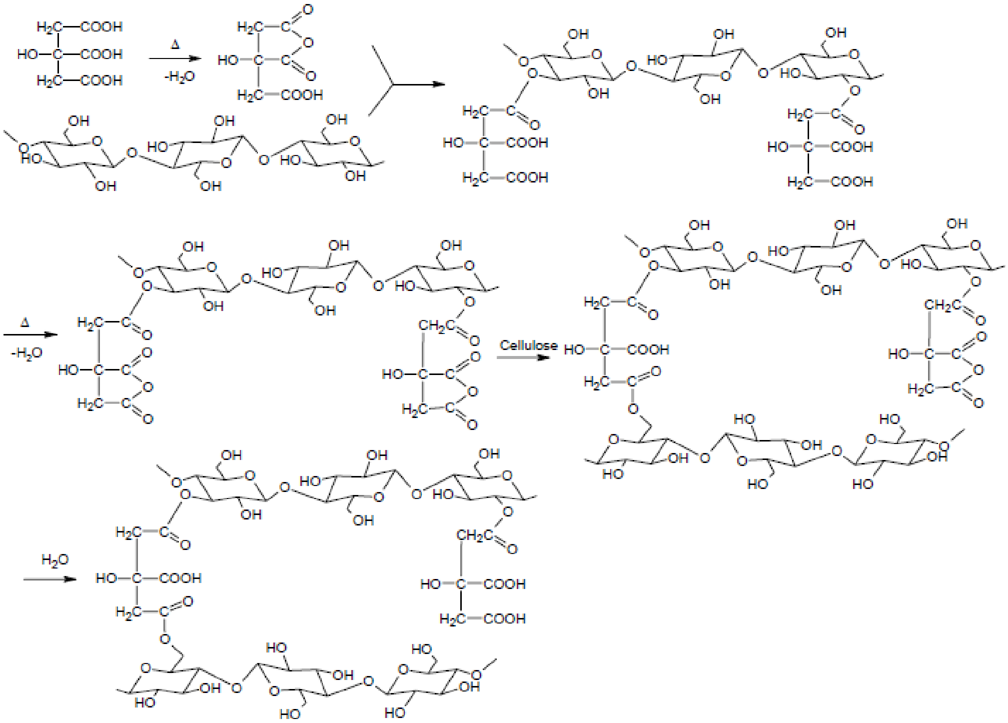


Fig.3: Thermo chemical reaction of papaya seed cellulose and citric acid

Effect of pH on adsorption: The batch equilibrium study with different pH values ranging from 3 to 7 were carried out at 30°C. Maximum percentage removal of Pb(II) adsorption on papaya seed were observed at pH 4. Little adsorption at lower pH for modified and unmodified papaya seed could be ascribed to the hydrogen ions competing with lead ions for adsorption site. At higher H^+ ion concentration, the adsorbent surfaces become more positively charged, thus reducing the attraction between adsorbent and metal ions. However, it was also observed that the adsorption capacity of lead ions decreased with further increase in pH due to the formation of anionic hydroxide which reduced the concentration of free lead ions. This result was relatively same with the previous study conducted by [6].

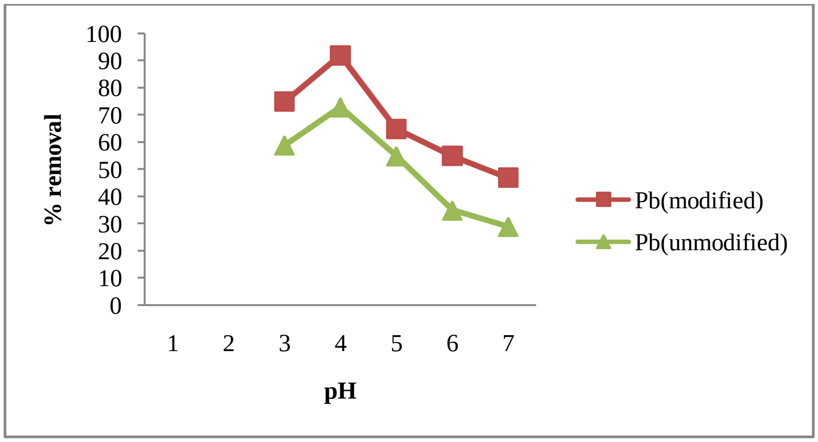


Fig.4: Effect of pH upon the % removal of lead(II) ions on modified and unmodified papaya seed

Effect of contact time on adsorption: The results shows that for an initial metal ion concentration of 30 ppm for Pb(II) ions, there was a progressive increase in the amount of metal ions bound as the contact time increased for both modified and unmodified substrate. After the contact time of 90 min, as the time increased further, the amount adsorbed reduces. This means that equilibrium was reached at 90 min, and the adsorption sites became saturated to maximum uptake capacity. The modified substrate was able to absorb more than the unmodified substrate. This was because the citric acid donated proton and made the adsorbent surface protonated and upon contact with the metal ions, it adsorbed more rapidly. This result was relatively same with the previous study conducted by [8].

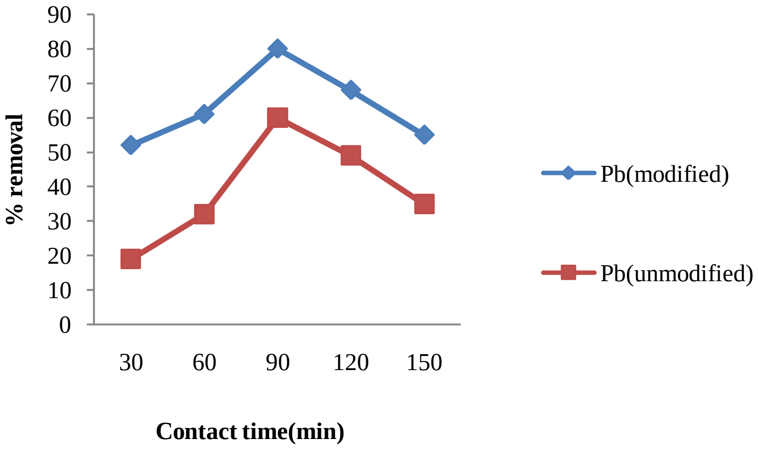


Fig.5: Effect of contact time upon the % removal of lead (II) ion on modified and unmodified papaya seed

Effect of equilibrium time on adsorption: The increase in initial Pb (II) concentration decreased the percent adsorption and increased the amount of uptake per unit mass of the adsorbent (mg g^{-1}).Although modified substrates was able to bind more Pb (II) ion than unmodified. This is as a result of the incorporation of carboxyl group by the citric acid on the adsorbent surface which enhances the binding ability of the sorbent and as such increasing the number of binding sites. This result was relatively same with the previous study done by [9].

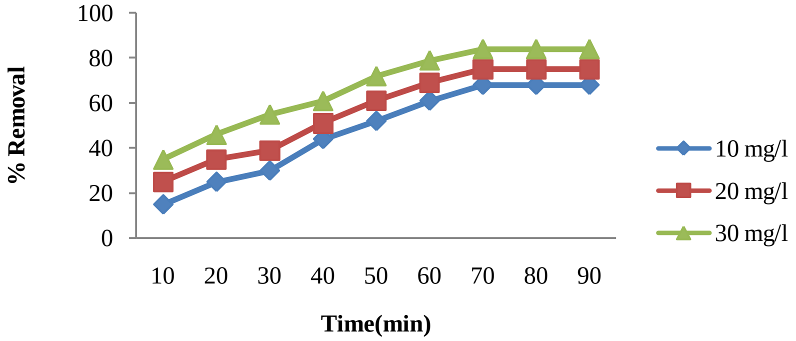


Fig.6: Percent removal of lead(II) ion at different time of agitation

Effect of adsorbent dose on adsorption: It was observed that percentage of lead ion removal increased with increase in adsorbent dose. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the adsorbent [**10]**.As the adsorbent dosage was increased from 0.5 to 1.5 g, the adsorption capacity get increased, but further increase of adsorbent dose from 1.5 to 2.5 decreases the adsorption capacity. This may be due to the decrease in total adsorption surface area available to lead ion resulting from overlapping or aggregation of adsorption sites. Thus with increasing the adsorbent mass the amount of lead ion adsorbed onto unit mass of adsorbent gets reduced, thus causing a decrease in q_e value with increasing adsorbent mass concentration. This result was relatively same with the previous study done by[**(11].**

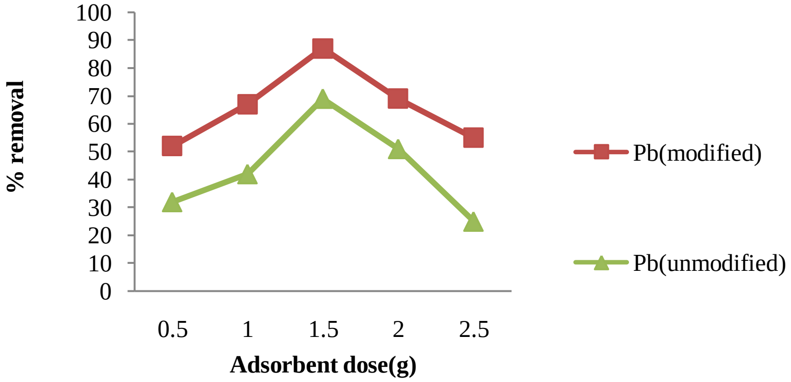


Fig.7: Effect of adsorbent dose upon the % removal of lead (II) ion on modified and unmodified papaya seed

Adsorption isotherm study: Langmuir isotherm was expressed as

$$C_e/q_e = 1/q_{max.}.b + C_e/q_o$$

Where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}), Ce is the equilibrium concentration (mg L^{-1}) and q_{max} (mg g^{-1}) and b are the Langmuir isotherm constants related to free energy. [12]

Freundlich isotherm was expressed as

$$\log q_e = \log k_F + 1/n \log c_e$$

Where K_F and n are Freundlich isotherms constant related to adsorption capacity and adsorption intensity and C_e is the equilibrium concentration of adsorbate solution. [12]
The Langmuir and Freundlich biosorption constants evaluated from the isotherms with the correlation coefficients are listed below. Equilibrium data agree well with the Langmuir model and Freundlich model.

Table.1: Langmuir isotherm constants for Pb(II) biosorption on modified and unmodified PS

Adsorbent	**Q_{max}**	**b**	**R^2**
Unmodified PS	0.2219085	9.79431	0.985
Modified PS	0.0065685	30.3030	0.997

Table.2: Freundlich isotherm constants for Pb(II) biosorption on modified and unmodified PS

Adsorbent	**K_f**	**n**	**R^2**
Unmodified PS	2.327	2.189141	0.998
Modified PS	0.2877	2.8409091	0.999

APPLICATIONS

The present study shows the applicability of unmodified and modified papaya seed for the removal of lead (II) ion from aqueous solution. Modification of papaya seed with citric acid increases the removal of lead ion. In a batch design, it has been shown that the modified papaya seed removes 95 % of the lead (II) ion as compare to unmodified papaya seed.

CONCLUSIONS

Citric acid modification improved the adsorption capacity of papaya seed probably due to higher number of active binding sites, better ion-exchange properties and formation of new functional groups that favours metal ion uptake. The lead biosorption performance on modified papaya seed is significantly affected by pH, adsorbent dose and contact time. The optimum pH value, adsorbent dose and contact time for lead(II) ion adsorption were found to be 4 , 1.5 g of adsorbent for 90 min respectively. The adsorption process followed the Langmuir and Freundlich model .The interactions between Pb(II) ions and functional groups on the surface of the biosorbent are confirmed by FTIR spectra and shows that carboxyl and hydroxyl groups are involved in Pb(II) ion binding to the modified papaya seed.

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