

# Comparative investigation on biosorption studies for removal of Pb (II) from aqueous solution using banana peels powder and orange peels powder

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## Abstract

This study focuses on understanding biosorption with an objective of exploring low-cost adsorbents using chemically activated banana and orange peels powder for removal of Pb (II) ions from the aqueous solution. The impacts of several environmental factors like pH, adsorbent dose, contact time and metal ion concentration have been analysed on the adsorption behaviour of the adsorbents. The activated adsorbents were characterised by Fourier transform infrared spectroscopy (FTIR). The effects of various parameters such as adsorbent dosages, contact duration, pH and metal ion concentration were investigated with help of batch experiment method.

Various isotherm models were employed to analyse and to interpret the experimental data. Among these, the Langmuir isotherm models were the most accurate in describing the adsorption behaviour of both adsorbents. This research would be significant because continuous research and development efforts are essential for improving the effectiveness of heavy metals adsorption process by banana and orange peels.

**Keywords:** Biosorption, Biowaste, Heavy metal removal, Lead (II) ion.

## Introduction

The economic development of a country largely depends on the industrialisation, but the environmental pollution is an inevitable price which is being paid for the development. Many industrial units directly discharge wastewater into local water bodies i.e. lakes, rivers and oceans without proper treatment and management strategies. Water pollution is an increasingly harmful global crisis to the Earth through irreplaceable human activities and is becoming an environmental, health, economic and planning issue in India as well as in other developing countries<sup>11</sup>.

Various pollutants like pesticides, chemicals, waste oil and heavy metals are regularly transported into water and impact the environment dreadfully which is becoming a potential threat to the aquatic life, human health as well as to the agriculture and this has been a matter of great concern due to their toxic nature and hazardous effects<sup>9</sup>. Environmental pollution by toxic heavy metal contamination due to rapid industrialization is a challenging problem for maintaining

the quality and hygiene of water<sup>21</sup>. Industrial effluents contain many heavy metals as crucial pollutants like chromium, zinc, lead, copper, iron, cadmium, nickel, arsenic and mercury<sup>6</sup>.

Most of these heavy metal pollutants are released by paint, dye, battery and chemical manufacturing units along with textile, pharmaceutical, paper, mining, electroplating, finishing of metal and fine chemical industries<sup>31</sup>. The heavy metals accumulation is developing a severe threat to public health and hazardous effect in environment due to their cumulative, toxic and non-biodegradable characteristics. These metals are known to be lethal and carcinogenic, causing substantial damage to aquatic ecosystems and human health. Health disorders may range from nausea and skin irritation to neurological dysfunction and cancer<sup>30</sup> and damage to the gastrointestinal, cardiovascular and renal systems, as well as peripheral and central nervous systems<sup>25</sup>. Wastewater treatment combines physical, chemical, and/or biological processes to remove solids, organic matter, nutrients, inorganic and organic pollutants from effluents.

The available techniques are classified into three classes: (i) conventional methods including coagulation/flocculation, precipitation, biodegradation, sand filtration and adsorption using commercial activated carbons (CAC); (ii) established recovery processes comprising of solvent extraction, evaporation, oxidation, electrochemical treatment, membrane separation, membrane bioreactors, ion-exchange and incineration and (iii) emerging removal technologies that include advanced oxidation - adsorption onto non-conventional materials, biosorption, biomass and nanofiltration. Adsorption/Biosorption offers the simplest method for eliminating organic compounds or metals from wastewaters, before discharging them into the environment<sup>28</sup>.

Conventional methods such as chemical precipitation, carbon adsorption, ion exchange, evaporation and membrane processes are found to be effective in removing of wastewater contaminants. Recently, biological treatments have gained popularity to remove toxic and other harmful substances. The agricultural and forestry waste, contributing to the environmental pollution while misusing biomass, are having a great potential of reuse due to their abundance, low cost, nontoxic and biodegradable nature. In fact, cultivation of agricultural crops and harvesting generate an abundant amount of waste (e.g. shells, straw) that can be used for wastewater treatment<sup>2</sup>.

Waste biomass may be used as an adsorbent in its original, raw form, modified bio-waste-based sorbents, or a source material for the synthesis of activated carbon adsorbents through carbonization. Many agricultural wastes due to the specific structure, chemical properties and presence of specific functional groups like aldehyde, carboxyl, ketone, alcohol and phenol groups in polymeric chains are responsible for high adsorption capacity of metals and organic compounds<sup>8</sup>.

Numerous attempts have been made to remove heavy metals by using agricultural residue as biosorbent such as agricultural byproduct *Humulus lupulus* (common hop) was used to remove Pb (II) upto 75%<sup>16</sup>. Chemical modified apple residue waste was used for removal of Pb (II) upto 80%<sup>10</sup>. Chemically modified sugarcane with succinic anhydride for removal of Cd (II), Cu (II), Pb (II) was investigated and removal was found more than 80%<sup>20</sup>. Agro waste of black gram husk was investigated for removal of Ni (II), Pb (II), Cd (II), Cu (II), Zn (II) upto 93%<sup>26</sup>. Waste tea leaves were used for removing Ni (II), Fe (II), Zn (II) upto 85.9%, 78% and 93%<sup>3</sup>. The use of rice straw, soybean hulls, sugarcane bagasse, peanut shells, pecan and walnut shells was investigated for removal of Cd (II), Pb (II), Cu (II), Zn (II), Ni (II) and the order of removal of heavy metal ions was found as Pb > Cu > Cd > Zn > Ni<sup>18</sup>.

Banana and orange peels are abundantly available and inexpensive. They contain mainly cellulose, pectin (galacturonic acid), hemicellulose, lignin, chlorophyll and other low molecular weight compounds. The residue of banana and orange can be processed and converted to be adsorbent because they have large surface areas, high swelling capacities, excellent mechanical strengths and are convenient to use and have great potential to adsorb harmful contaminant such as heavy metals<sup>19</sup>.

In the present study, activated banana and orange peels powder were used to remove lead from wastewater. Lead contamination must be removed critically to protect people's health and lives. Exposure to lead in drinking water can have severe and prolonged health complications, particularly in women and children<sup>22</sup>. Even low concentrations of lead exposure can cause growth-related setbacks, reduced IQ and behavioural challenges in children. For adults' kidney damage, reproductive problems and high blood pressure are prominent diseases<sup>14,27</sup>. Various industries such as batteries, paint, plastic, automobile, steel etc. contribute significantly to this increased level of lead in water<sup>12</sup>.

## Material and Methods

**Chemical reagent:** 1000 mg'/L of Pb (II) solution was prepared by dissolving 1.5986 g of Pb (II) nitrate in 200 ml of distilled deionized water in a beaker followed by the addition of 1.5 ml of concentrated nitric acid (HNO<sub>3</sub>). Then this solution was transferred into 1L volumetric flask and diluted to the mark with distilled water. Solutions with varying metal ion concentrations from 25 to 300 ppm were

prepared with the help of the stock solution. 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) were used to adjust the pH values of the solutions.

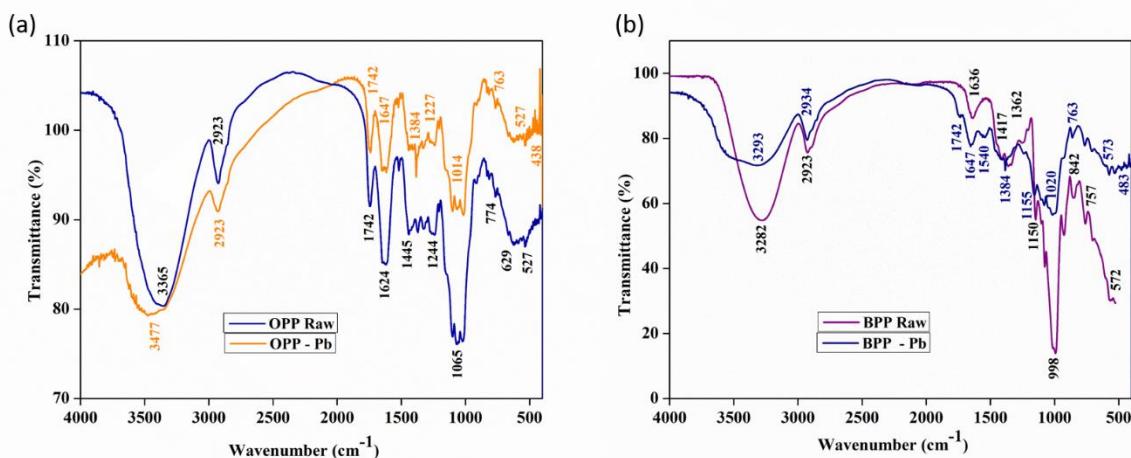
**Preparation of adsorbent:** We collected banana and orange peels from various juice centres. The peels were washed several times with distilled water. First, we dried them 1st in sunlight and then in an oven at 100°C for 24 hrs. The banana and orange peels were later cut into small pieces and half of the peels were converted into powder form. After drying, the powder was sieved. The particle sizes were 1 to 5 mm. We prepared 1.6-gram silver nitrate solution in 100 ml of water. We took 30 grams of fruit peels powder and 30 grams of dried fruit peels each. We made a purifying set up in plastic bottle starting from bottom pebbles-cotton- filter paper-banana/orange peels or powder- cotton<sup>5,30</sup>.

## Characterisation of adsorbent

**FTIR:** FTIR was used to identify the main functional groups available on the adsorbent surface. Raw BPP, OPP and Pb-BPP, Pb-OPP were analysed to investigate functional groups by FTIR spectra and to determine the optimal adsorbent before and after the adsorption through FTIR analysis. A broad and distinct peak at 3282 cm<sup>-1</sup> in the FTIR spectrum of BPP raw shows the presence of O-H stretch, a peak at 2923 cm<sup>-1</sup> indicates C-H stretching and 1742 cm<sup>-1</sup> peak represents C=O stretching of the aldehyde group. 1636 cm<sup>-1</sup> specifies C=C stretching and peaks at 1417 cm<sup>-1</sup>, 1362 cm<sup>-1</sup> and 1150 cm<sup>-1</sup> confirm -CH<sub>2</sub> bending, -OH bending and -C-O stretching, 998 cm<sup>-1</sup>, 842 cm<sup>-1</sup> 757 cm<sup>-1</sup> peaks specify vinyl bending, aromatic C-H mono and di substitution bending respectively. The intensity and position of above peaks are changed after the adsorption of lead by raw BPP as shown in the fig. 1. This signifies the involvement of the above stated group for binding Pb<sup>+2</sup> metal ion.

After the adsorption of lead, the stretching band of -O-H group at 3282 cm<sup>-1</sup> is shifted to 3293 cm<sup>-1</sup> and became broader, C=O peak and C=C peaks also shifted and became less intense and 998 cm<sup>-1</sup> peak disappeared after the adsorption of Pb<sup>+2</sup>. The red shift of O-H bending from 1384 cm<sup>-1</sup> to 1362 cm<sup>-1</sup> is associated with the involvement of the hydroxyl group in the hydrogen bonding network. A broad and distinct peak at 3365 cm<sup>-1</sup> in the FTIR spectrum of OPP raw shows the presence of O-H stretch, a peak at 2923 cm<sup>-1</sup> indicates C-H stretching and 1742 cm<sup>-1</sup> peak represents C=O stretching of the aldehyde group. 1624 cm<sup>-1</sup> specifies C=C stretching and peaks at 1445 cm<sup>-1</sup>, 1244 cm<sup>-1</sup> and 1065 cm<sup>-1</sup> confirm -CH<sub>2</sub> bending, -OH bending and -C-O stretching, 774cm<sup>-1</sup> and 629cm<sup>-1</sup> peaks specify aromatic C-H mono and di substitution bending respectively.

After the adsorption of lead, the stretching band of -O-H group at 3365 cm<sup>-1</sup> is shifted to 3477 cm<sup>-1</sup> and became broader, C=O peak and C=C peaks also shifted and became less intense and a peak at 1065 cm<sup>-1</sup> shifted to 1014 cm<sup>-1</sup> and became less intense which signifies the involvement of C-O in binding of Pb<sup>+2</sup>.



**Fig. 1: (a) FTIR before and after Pb (II) adsorption by OPP (b) FTIR before and after Pb (II) adsorption by BPP**

The red shift of O-H bending from  $1244\text{ cm}^{-1}$  to  $1227\text{ cm}^{-1}$  is associated with the involvement of the hydroxyl group in the hydrogen bonding network<sup>4</sup>. New peaks emerged in FTIR of  $\text{Pb}^{+2}$  adsorbed BPP and OPP at  $483\text{ cm}^{-1}$  and  $438\text{ cm}^{-1}$  represent Pb-O stretching vibrations.

**Batch adsorption studies:** Batch adsorption studies were performed to determine the effect of one of the parameters discussed in table 1 i.e. pH (1 to 12), adsorbent dose (2 to 20) g, metal concentration (25, 50, 75, 100, 150, 200, 250 and 300)  $\text{mg L}^{-1}$ , contact time (5, 10, 20, 40, 60, 80, 100, 110, 120, 150 and 180) min and particle size (150 m) by keeping other parameters constant simultaneously. After every test series, metal-containing solutions were allowed to settle and any leftover metal-ion solutions were filtered through Whatmann no. 42 filter paper. 20 millilitres of each sample was stored in for the purpose of examining residual Pb (II).

Atomic absorption spectroscopy was used to determine the concentration of the remaining Pb (II) ion after the experiment. The percentage of metal adsorption (in %) by adsorbents is determined by the following equation (1):

$$\% \text{ Removal of Pb (II)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where  $C_0$  is initial metal ion concentration and  $C_e$  is the concentration.

**Adsorption isotherm:** According to Langmuir's theory, the saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (2)$$

Equation (2) can be rearranged by following linear form:

$$\frac{C_e}{q_e} = \frac{1}{b q_{\max}} + \frac{1}{q_{\max} C_e} \quad (3)$$

where  $C_e$  is the equilibrium concentration,  $q_e$  is the amount of metal ion adsorbed,  $q_{\max}$  is  $q_e$  for a complete monolayer

( $\text{mg L}^{-1}$ ) and  $b$  is the sorption equilibrium constant ( $\text{L mg}^{-1}$ ). A graph of  $C_e$  versus  $C_e/q_e$  should indicate a straight line of slope  $1/q_{\max}$  and an intercept of  $1/bq_{\max}$ .

Freundlich has found that if the concentration of solute in a solvent at equilibrium  $C_e$  ( $\text{mg L}^{-1}$ ) was raised to the power of  $m$ , the amount of solute adsorbed being  $q_e$ , then  $C_e/q_e$  was found to be constant at a given temperature. This satisfactory empirical isotherm can be used for non-ideal sorption and is expressed by the following equation in the form of a logarithm of both sides<sup>29</sup>.

$$\log q_e = \log K_f + m \log C_e \quad (4)$$

An adsorption isotherm is characterized by a certain constant, the value of which expresses the surface properties and affinity of the sorbent and can also be used to compare the bio-chemosorptive capacity of biomass for different metal ions. Out of several isotherm equations, two have been applied for this study i.e. Freundlich and Langmuir isotherms<sup>7</sup>.

## Results and Discussion

**Effect of concentration of Pb (II) ion:** The concentration of the Pb (II) metal ion ranged from 25 to 300  $\text{mg/L}$  for adsorption studies. Other variables such as the amount of adsorbent used ( $10\text{ g L}^{-1}$ ), contact period (90 min.) and pH 8, were kept constant. As the concentration of metal ions increases, the percentage of adsorption decreases, as illustrated in figure 2 (a). This behaviour could be due to the constant number of available active sites on the adsorbent. Here, the amount of adsorbent is constant. Consequently, Pb (II) ions remain unabsorbed in the solution due to the saturation of binding sites on the available adsorbent.

For OPP, Pb (II) ion removal efficiency falls from 87.3 to 74.2% and for BPP it falls from 82.6 to 71.2%. It may be because surface area availability to hold the original large number of ions decreases with increasing metal ion concentration<sup>15</sup>. This means that ions and sorption sites interact more often at lower levels to make removal more efficient.

**Effect of contact time:** The experiments were conducted with varying the contact period from 20 to 180 minutes while maintaining constant values for other parameters such as pH 8, Pb (II) metal ion concentration of 25 mgL<sup>-1</sup>, adsorbent dose of 10 gL<sup>-1</sup> and biomass particle size of 150  $\mu$ m. The findings, as illustrated in figure 2 (b), reveal that removal effectiveness rises as contact duration increases because more time is given for metal ions to interact with biosorbents. However, the contact time does not show its impact after 90 minutes because the 90-minute effective period has already elapsed.

**Effect of adsorbent dosage on removal efficiency:** The effect of biosorbent dosage on the removal of Pb (II), with dose ranging from 2 to 20 gL<sup>-1</sup> and other factors such as pH, contact period and metal ion concentration kept constant is illustrated in fig. 2 (c). The processes were applied using orange peel powder (OPP) and banana peel powder (BPP) with biomass dosages ranging from 2 to 20 gL<sup>-1</sup>. The identical conditions were applied to both adsorbents. The removal efficiency increases with the adsorbent's biomass. The increase in adsorption with an increase in adsorbent surface area and the availability of additional adsorption sites<sup>23</sup>. The

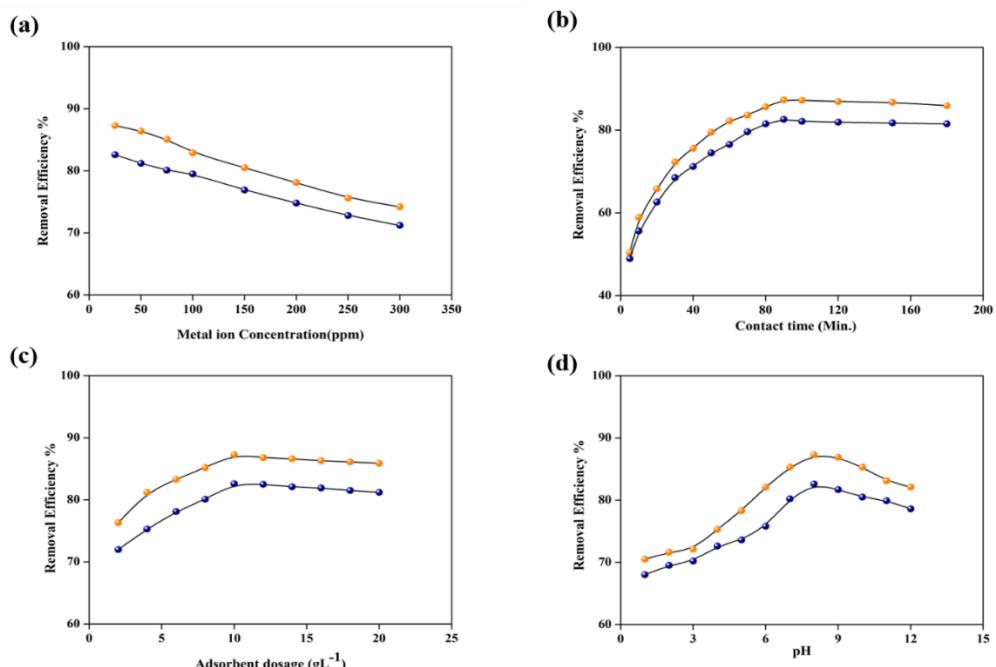
highest removal efficiencies of OPP and BPP have been found to be 87.3% and 82.6% respectively on 10 gL<sup>-1</sup> adsorbent dosage each.

**Effect of pH:** Pb (II) ion adsorption from OPP and BPP was carried out independently with pH changes from 2 to 12 while other factors such as adsorption dosage (10 gL<sup>-1</sup>), Pb (II) concentration (25 mgL<sup>-1</sup>) and time (90 minutes), were held constant. Maximum removal of Lead ion was at pH 8 i.e. 87.3% for OPP and 82.6% for BPP. Hydrogen ions become less abundant when pH rises. Thus, the interaction between metal and hydrogen ions also gets reduced and the removal of metal ions increases as shown in fig 2 (d)<sup>17</sup>.

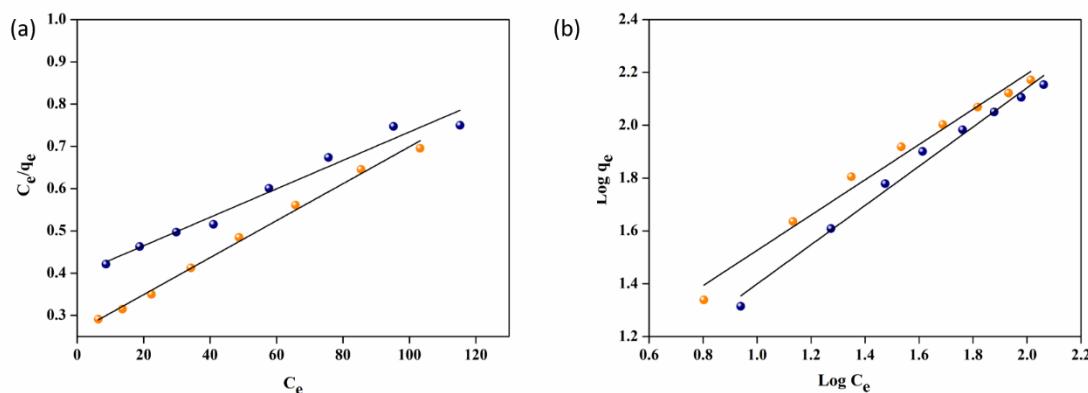
**Isotherm models of the Biosorption:** The distribution of Pb (II) ions between two contacting phases is described mathematically by isotherm models. The distribution of both biosorbents (OPP and BPP) between the liquid and solid phases depends on how much the Pb (II) metal ion attracts them. The Langmuir and Freundlich isotherms were used to explain the experimental data as shown in figure 3 (a) and (b). The isotherm model parameters were estimated from fitting of experimental point of Pb (II) adsorption as reported in table 2<sup>13,24</sup>.

**Table 1**  
**Experimental conditions**

Experimental conditions	Ms (gL <sup>-1</sup> )	pH	Ps ( $\mu$ m)	T (min.)	C <sub>o</sub> (mgL <sup>-1</sup> )
Effect of adsorbent dosage Ms (gL <sup>-1</sup> )	2-20	8	150	90	25
Effect of pH	10	2-12	150	90	25
Effect of contact time T (min.)	10	8	150	0-180	25
Effect of concentration of Pb (II) ion C <sub>o</sub> (mgL <sup>-1</sup> )	10	8	150	90	25-300



**Fig. 2:** (a) Effect of metal ion concentration on removal of Pb (II) ions, (b) Effect of contact time on removal of Pb (II) ions using OPP and BPP, (c) Effect of biomass dosage on removal of Pb (II) ions and (d) Effect of pH on removal of Pb (II) ions using OPP and BPP



**Fig. 3: (a) Langmuir adsorption isotherm for OPP and BPP, (b) Freundlich adsorption isotherm for OPP and BPP**

**Table 2**  
**Langmuir and Freundlich isotherms model parameters**

Adsorbent	Langmuir isotherms			Freundlich isotherm		
	R <sup>2</sup>	q <sub>max</sub> mg g <sup>-1</sup>	b, L mg <sup>-1</sup>	R <sup>2</sup>	K <sub>f</sub> , mg g <sup>-1</sup>	m
OPP	0.9953	294.27	0.0168	0.9840	7.21	0.6678
BPP	0.9734	227.11	0.0085	0.9888	4.53	0.7429

## Conclusion

The following conclusions are drawn from the above results and discussion:

1. Both orange peel powder (OPP) and banana peel powder (BPP) can be applied as adsorbent for the removal of Pb (II) metal ions from textile and dye effluents.
2. The maximum adsorption was found 87.3 % for OPP and 82.6% for BPP at pH 8 with contact time 90 min.
3. Orange peel powder (OPP) has been found as more efficient biosorbent for the removal of Pb (II) from wastewater as compared to banana peel powder (BPP).
4. The experimental results have been analysed by Langmuir and Freundlich isotherms models. The adsorption data were found to be best fitted with Langmuir adsorption isotherms, thus indicating the applicability of monolayer coverage of the Pb (II) on the surface of the adsorbent.

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