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***Research Paper***

# Biosorptive Nickel Removal by Fruit Peel Waste: Batch, Kinetic and Isotherm Studies

***Sonali R. Dhokpande[1], Jayant P. Kaware[2]**
[1] Department of Chemical Engineering, Datta Meghe College of Engineering, Airoli, Navi Mumbai, (MS), 400708, INDIA
[2] Bhonsala Institute of Engineering and Research, Akola, Maharashtra, 444001, INDIA

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***Abstract:*** *Heavy metal removal can be carried out by physical, chemical and biological methods. The most common methods used for heavy metal removal include adsorption, ion exchange, electro dialysis, membrane separation, activated sludge process, trickling filters, precipitation, coagulation etc. Each method has certain advantages and disadvantages. The selection of suitable methods depends on effluent quality and quantity, recoverability, economy and prescribed regulatory limits. Use of waste material for waste water treatment is widely explored area of investigation. There is scope for improvement in heavy metal treatment due to availability of wide variety of waste material. The current investigation is aimed at studying the ability of fruit peel waste for removal of heavy metal. From literature it was found that the waste containing pectin has ability to accumulate nickel. In this research high pectin waste namely Orange, banana and Mosambi fruit peel waste were analyzed for its ability to remove nickel from synthetic effluent. For all three sorbent materials initially steep fall in concentration was observed in initial increase in adsorbent dosages upto 6 grams. It was observed that the nickel uptake followed Freundlich isotherm with $R^2$ value of 0.932. The constant n and k in Freundlich equation were found to be 0.219 and $5.70 \times 10^{-12}$ respectively. The Langmuir isotherm was found unsatisfactory for describing the nickel uptake with $R^2$ value of 0.810. The Nickel uptake follows both first and second order kinetics with $R^2$ values more than 0.96 for all sorbent materials.*

**Keywords:** nickel, biosorption, kinetics, isotherm, fruit peel.



## Introduction

The presence of heavy metal in the industrial effluent is a major concern from environmental and health perspectives. Heavy metals like nickel, cadmium, chromium, iron, platinum, arsenic etc. are cause of concern for the industries like catalyst, batteries, petroleum and refinery, electroplating, mining, paint, fertilizer, leather[1,2]. These heavy metals may have adverse effect on man and environment if present in excess. The adverse effect of nickel includes lung cancer or nasal tumors. Dermatitis is developed upon skin contact [3,4]. Nickel is present in the effluent from batteries, catalyst, petroleum and electroplating industry[5,6]. Nickel inhalation poses greater risk than nickel in water. The nickel removal can be carried out several techniques such as adsorption, ion exchange, electro dialysis, membrane separation, activated sludge process, trickling filters, precipitation, coagulation etc.[7,8]. Treating waste by using waste is modern day philosophy in environmental research. Adsorption adopts this philosophy to a great effect. Few biological methods are found effective for nickel removal. Use of domestic waste has potential to form complex with heavy metal such as nickel and help sorptive nickel treatment [9, 10].

Krishna and Swamy focused on the use of powder of Mosambi fruit peelings (PMFP) for nickel removal [11]. They also studied the influence of affecting parameters. They observed that optimum pH was 6 and equilibrium time was 90 minutes for nickel removal. Correlation Coefficient($R^2$) was found to be 0.9962 for Langmuir isotherm indicating excellent agreement. Freundlich isotherm was also satisfactory with $R^2$ value 0.94. Sha et. al. used orange peel xanthate for heavy metal removal from solution[12]. They pretreated 50 grams of orange peels with ethanol and sodium hydroxide and studied the affecting parameters for heavy metal removal. The sorption data followed Langmuir isotherm and second order rate kinetic model. Amiri et. al. explored the adsorption potential of laeagnus angustifolia fruit powder for the removal of heavy metals[13].They performed experiment to study the effect of parameters like pH, sorbent amount, initial metal ion concentration and contact time on Nickel removal They observed optimum pH of 2 and optimum contact time required was observed to be 70 minutes. Al-Azzawi et. al. carried out an research on zinc, chromium and nickel removal by using Banana peels[14]. They found maximum removal at pH 5 and 60 minutes. Seshadri et. al. removed nickel metal ions from aqueous solution by using citric acid modified *Annona squamosa* bark powder[15]. They studied the effect of pH, adsorbent dose and initial concentration of metal solution and contact time on nickel removal. Sorption data followed Langmuir isotherm with pseudo-second kinetic model. Abbasi et.al used Banana peel as waste biomaterial for adsorption of cobalt and nickel[16]. They observed the maximum removal of metal ions at pH 5.5. As Banana peel dose increased from 1 to 3 g/L, the adsorption increased. Maximum rate of removal occurred within 3 min. Leaf powder was used to adsorb nickel by Kumar and Kirthika[17]. An influence of various parameters on adsorption was studied by them. They also investigated kinetics of adsorption and applied to model the kinetics of nickel adsorption onto bael tree powder (BT leaf powder). Langmuir, Freundlich and Temkin equations were used for analyzing the data. They obtained maximum 60.21% removal for nickel. Pseudo-second-order rate equations described the kinetics of adsorption. The BT leaf powder was found to have high potential for the removal of $Ni^{2+}$ from wastewater. Muthusamy et.al. used maize cobs as an adsorbent for nickel removal[18]. They studied effect of parameters like initial concentration, adsorbent dosage, contact time and agitation speed on nickel removal. They observed an increase in the adsorption initially with increase in adsorbent dose. The biosorption percentage increased with dosage of biosorbent upto certain level. The contact time of 90 minutes was needed to achieve equilibrium. They also observed that Freundlich isotherm fitted better than Langmuir. An investigation on various pectin rich fruit wastes as biosorbents was carried out by Schiewer and Patil [19]. Kinetic and equilibrium studies for removal of various metals from effluent were carried out in this investigation. They observed that solute uptake followed second order model. 30-90 minutes were required to reach equilibrium. Also Langmuir isotherm was followed by equilibrium data.

## Material and Methods

**Preparation of Nickel Synthetic solution:** 8.94gm of nickel sulphate was dissolved in distilled water and total volume made upto 2000ml. The stock solution contains 1000 mg/liter of nickel. Standard nickel solutions were prepared by appropriate dilution of stock solution. The nickel solutions of different concentrations ranging from 5 to 60 mg/liter were prepared by appropriate dilution.

**Biosorbent preparation:** Experiment was carried out to assess the sorption capacity of two materials namely orange, mosambi and banana fruit peel waste. Fruit peel waste was collected from nearby juice center. It was chopped to finer size of 0.3 to 0.5 cm.

**Batch Experiment:** Experiment was carried out to assess the sorption capacity of three materials namely orange, mosambi and banana fruit peel waste. Fruit peel waste was collected from nearby juice center. It was chopped to finer size of 0.3 to 0.5 cm. Experiments were carried out at various amounts of sorbent material dosage.100 ml of synthetic effluent was taken in 250 ml conical flask. The known quantity of sorbent was added as per batch requirement. The flasks were stirred. The samples were analyzed after every 30 minutes interval after filtration until equilibrium was achieved. For studying the effect of contact time, five samples, with initial concentration 1000 mg/l of 100ml were taken in 250ml conical flask and 6 gms of sorbent material was added. The flasks were stirred. The samples were analyzed after each half hour interval.

## Results and Discussion

**Effect of sorbent dosages on Nickel Removal**: For studying the effect of sorbent dosage, five samples of 100 ml were taken in 250ml conical flask and 2, 4, 6, 8,10 and 12 gms of sorbent material was added to each sample. Experiments were conducted till equilibrium. Fig.1 and 2, indicates effect of nickel sorbent dosages on nickel concentration and percent nickel removal. For initial concentration of 1000 mg/liter final concentration after 8 hours was observed to be 431, 325 and 341 mg/liter for orange peel, mosambi peel and banana peel respectively. For all three sorbent materials initially steep fall in concentration was observed in initial increase in adsorbent dosages upto 6 grams. Gradually the concentration decreases and reaches equilibrium value. For the increasing in adsorbent dosage from 2 to 6 grams the corresponding increase in nickel removal was 21%, 31% and 31% for orange peel, mosambi peel and banana peel sorbent material. For next 6 to 10 grams the corresponding decrease was observed to be 5%, 15% and 13% respectively for these materials. Increasing adsorbent dosages provides higher surface area with further addition of dosage the solution becomes dense and all the adsorbent material cannot be utilized effectively. Figure 3 shows the percentage incremental rise in Nickel removal with increase in sorbent dosages.

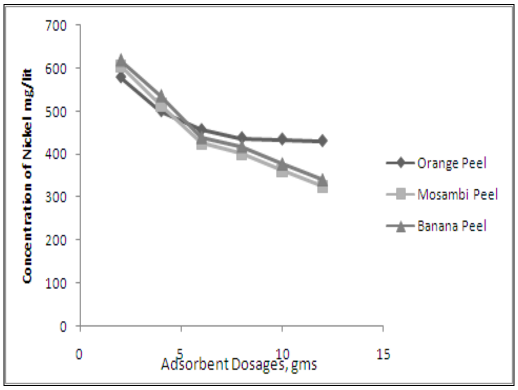


**Figure 1: Effect of sorbent dosages on nickel concentration**

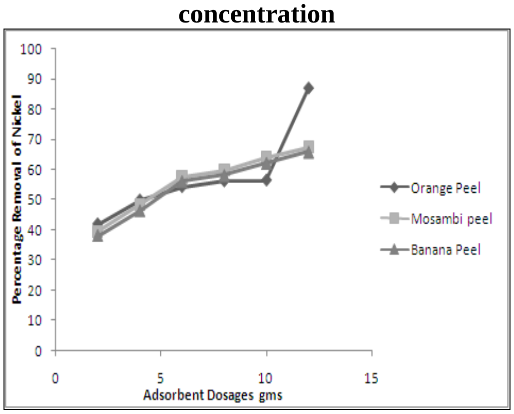


**Figure 2: Effect of sorbent dosages on percentage nickel removal**

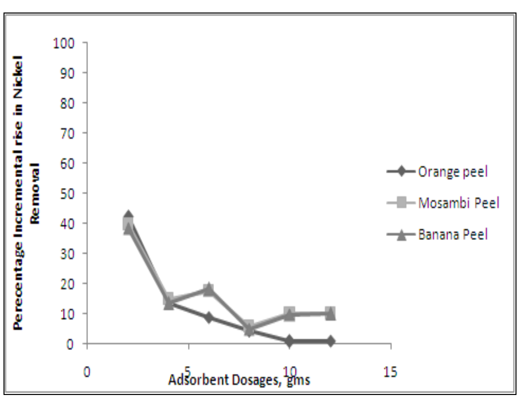


**Figure 3: Effect of sorbent dosages on incremental rise in percentage nickel removal**

**Effect of contact time on Nickel Removal**: Figure 4, 5 and 6 shows the effect of contact time on nickel biosorption expressed as final nickel concentration, percentage nickel removal and incremental nickel removal. For studying the effect of contact time, five samples, with initial concentration 1000 mg/l of 100ml were taken in 250 ml conical flask and 6 gms of sorbent material was added. The flasks were stirred. The samples were analyzed after each half hour interval. As shown in figure 4, it was observed that the optimum contact time for orange peel biosorbent is 120 minutes. The contact time for mosambi and banana peel was observed to be 150 minutes each. For the increasing in contact time from 15 to 100 minutes the corresponding increase in nickel removal was more than 10 percent for orange peel, mosambi peel and banana peel sorbent material. For next 100 to 180 minutes the corresponding nickel removal was less than 6 percent. It can be seen that the optimum contact time of 120 minutes was sufficient for these adsorbents. For increase in contact time from 120 minutes to 180 minutes, corresponding rise in percentage nickel removal was 3, 4 and 5 percent only. For orange peel initial sharp rise in the nickel removal can be because of higher affinity of nickel towards the specific biosorbent.

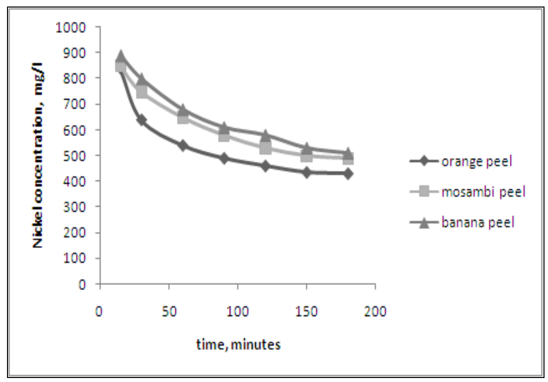


**Figure 4: Effect of contact time on nickel concentration**

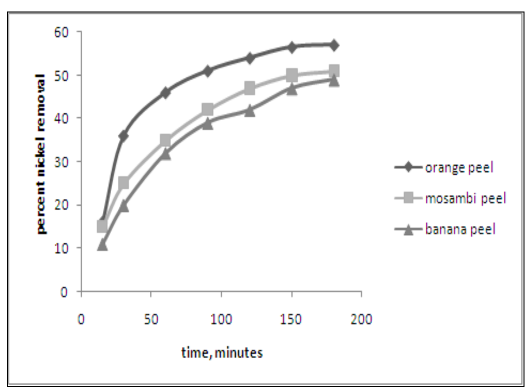


**Figure 5: Effect of contact time on percentage nickel**

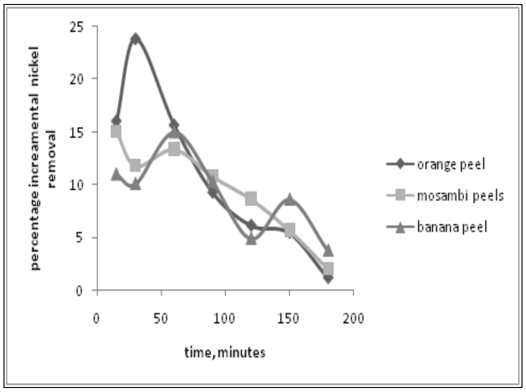


**Figure 6: Effect of contact time on incremental percentage nickel removal**

**Isotherm**

Freundlich isotherm is given by the empirical equation:

$$\frac{x}{m} = KC^{*1/n}$$

$$\ln\frac{X}{M} = \ln k + \frac{1}{n}\ln C^*$$

*X* is the amount of adsorbate adsorbed and *m* is the amount of adsorbent. *X/M* is the adsorbent loading, *C** is the equilibrium concentration of phenol, *k* and n are constants.

The Langmuir isotherm equation predicting monolayer physical adsorption is described as

$$q_e = \frac{q_0\ b\ C*}{1+bC*}$$

Where $q_e$ is adsorbent loading(X/M), $q_{0,}$ maximum adsorption capacity.The plot of ln 1/X/M verses ln 1/C* was plotted to fit the data in Langmuir equation.

Freudlich and Langmuir isotherms for orange peel are shown in fig.7 and 8 respectively. It was observed that the nickel uptake followed Freundlich isotherm with $R^2$ value of 0.932. The constant n and k in Freundlich equation were found to be 0.219 and 5.70 X $10^{-12}$ respectively. The Langmuir isotherm was found unsatisfactory for describing the nickel uptake with $R^2$ value of 0.810. The results of isotherm indicate that the uptake of nickel by biosorbent is monolayer adsorption. The Freundlich and Langmuir isotherm plots for mosambi peel are shown in fig.9 and 10 respectively. It can be seen from the figures, the nickel uptake follows both the isotherms satisfactorily with $R^2$ values above 0.93. The constants n and k in Freundlich equation were found to be 0.498 and 4.59 X $10^{-5}$ respectively. In case of banana peels, the experimental data was in excellent agreement with both the isotherms with $R^2$ values exceeding 0.95 in both cases. The constants n and k in Freundlich equation were found to be 0.489 and 3.46 X $10^{-5}$ respectively. Isotherms for banana peels are shown in fig. 11 and 12.The results for all the three materials indicate that the nickel removal followed Freudlich isotherm in all cases. The sorption is predicted to be monolayer for all three sorbent materials. The agreement with Langmuir equation in two cases indicates that physical as well as chemical bonding may be involved in the removal mechanism. In similar investigation Krishna and Swami also observed that the solute uptake of nickel followed both the isotherms [R1].

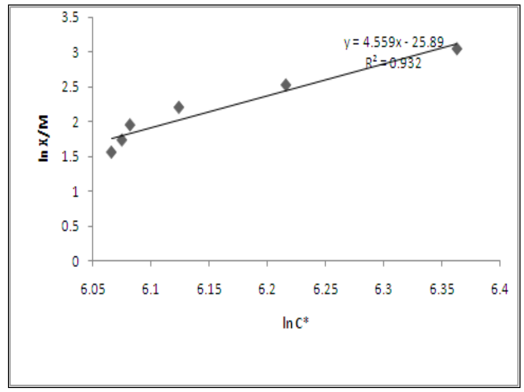


**Figure 7: Freundlich Isotherm for Orange Peel**

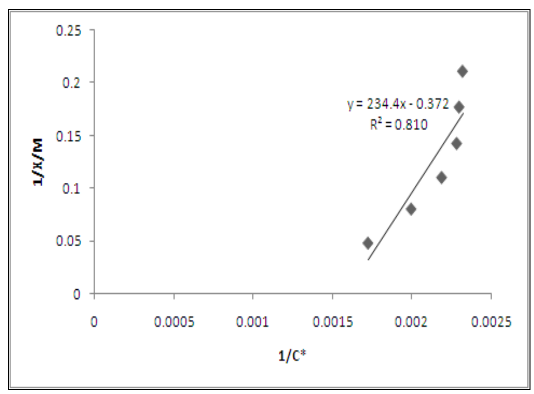


**Figure 8: Langmuir Isotherm for Orange Peel**

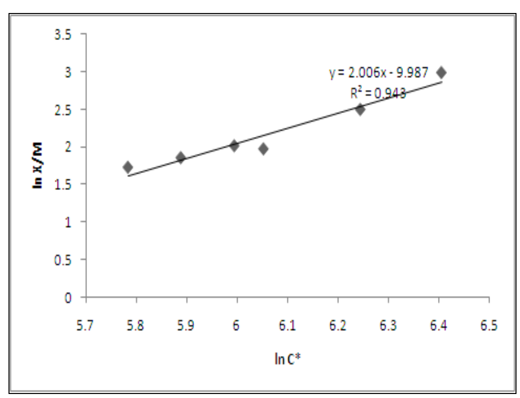


**Figure 9: Freudlich Isotherm for Mosambi Peel**

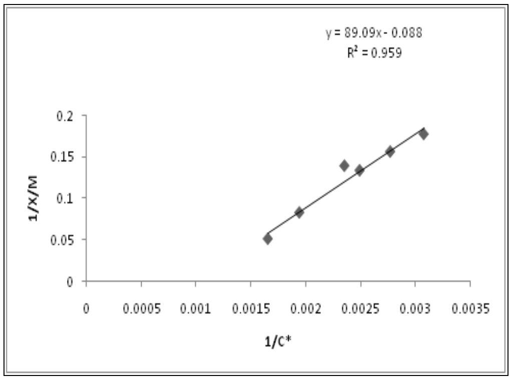


**Figure 10: Lagmuir Isotherm for Mosambi Peel**

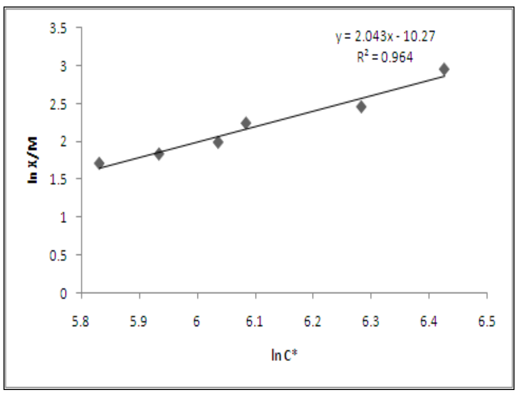


**Figure 11: Freudlich Isotherm for Banana Peel**

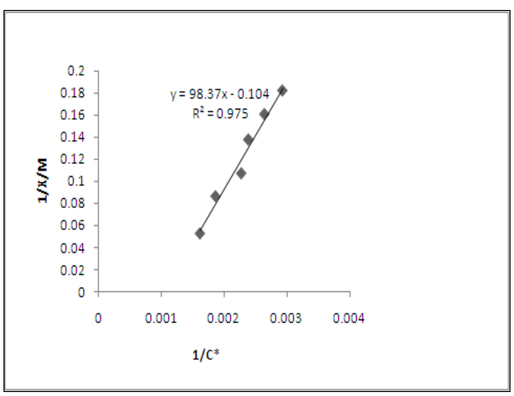


**Figure 12: Langmuir Isotherm for Banana Peel**

**Kinetics**

First order equation for sorption kinetics is written as

$$\ln (qe - qt) = \ln qe - k1t$$

where *qe* is the mass of metal ion adsorbed at equilibrium (mg/g), qt is the mass of metal adsorbed at time *t* (mg/g), *k*1 is the first order reaction rate constant. The Nickel uptake follows both first and second order kinetics with $R^2$ values more than 0.96 for all sorbent materials. The values of first order rate constants for the three adsorbents were observed to be 0.020, 0.024 and 0.028 respectively for BPB, MPB and OPB.

Second order equation for sorption kinetics is expresses as

$$\frac{t}{q_t} = \frac{1}{k_2}\frac{1}{qe^2} + \frac{t}{qe}$$

where *k*2 is the second order reaction rate constant. Values of maximum sorption capacity $q_e$ were estimated to be 11.76, 11.76 and 11.11 mg/g V. *k*2 values of were estimated to be 0.316, 0.153 and 0.216 (g/mg. min) respectively for BPB, MPB and OPB. A plot of *t*/*qt* against t is a linear relation for the second order kinetics. Figure 13 and 14 depicts first and second order kinetics for the biosorbents.

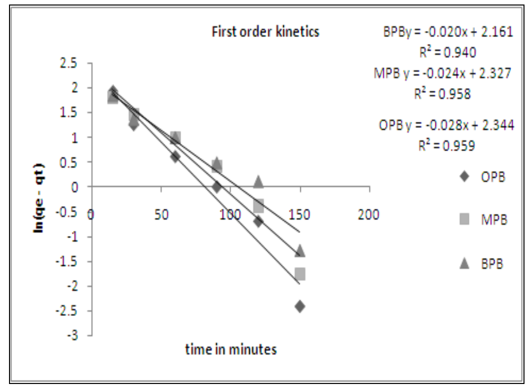


**Figure 13: First order kinetics**

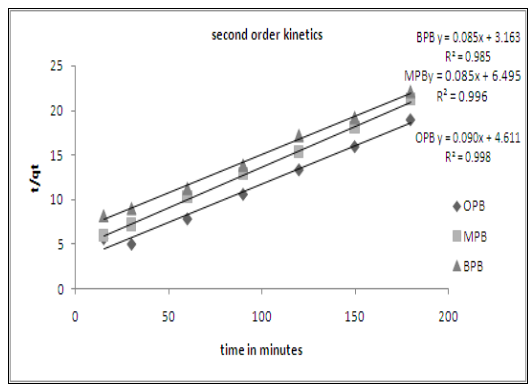


**Figure 14: Second order kinetics**

**Conclusion**

Treating waste by using waste is modern day philosophy in environmental research. Adsorption adopts this philosophy to great effect. Few biological methods are found effective for nickel removal. Use of domestic waste has potential to form complex with heavy metal such as nickel and help sorptive nickel treatment. For all three sorbent materials initially steep fall in concentration was observed for initial increase in adsorbent dosages upto 6 grams. The optimum contact time for three biosorbents was observed to appximately 120 minutes. It was observed that the nickel uptake followed Freundlich isotherm with $R^2$ value of 0.932. The constant n and k in Freundlich equation were found to be 0.219 and 5.70 X $10^{-12}$ respectively. The Langmuir isotherm was found unsatisfactory for describing the nickel uptake with $R^2$ value of 0.810. The Nickel uptake follows both first and second order kinetics with $R^2$ values more than 0.96 for all sorbent materials. The removal of nickel was maximum for orange peel biosorbent followed by mosambi peels and banana peels.

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