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Experimental study on adsorption of Nickel(II) from wastewater by agrowaste.

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ABSTRACT
In this study, the use of discarded banana and papaya stem as a biosorbent to remove nickel (II) ions from aqueous solutions is investigated. The effects of solution pH, biosorbent dose, initial metal concentration, contact time, and temperature were investigated in batch studies using activated carbon made from banana stem (BSAC) and papaya stem (PSAC) as the adsorbent. The goal was to identify the ideal biosorption conditions. Adsorption isotherm investigations demonstrated that, when compared to the Freundlich isotherm model, the Langmuir isotherm model provided a better fit for the experimental data. The maximal nickel removal capacity of the BSAC and PSAC adsorbents was 4.9019 mg/g and 5.181 mg/g, respectively. The findings of the current study imply that agricultural waste, such as papaya and banana stem waste, and can be employed in a useful way to remove nickel from aqueous solution.
KEYWORDS: biowaste, biosorbent, papaya stem.

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I. INTRODUCTION

Heavy metals have been released into the environment as a result of environmental contamination brought on by industrialization and the excessive use of chemicals worldwide. Due to their high toxicity, mobility in the environment, and lack of biodegradability, the presence of heavy metals in the environment is a significant issue that needs to be handled in the modern world.

[1] Heavy metal-containing wastewater disposal can harm human health and degrade water quality in terrestrial and aquatic environments. A poisonous, non-biodegradable metal with an atomic number of 28, nickel is shiny and silvery in appearance. High nickel intake can result in negative health effects such birth defects, cancer, respiratory failure, hepatitis, skin rashes, kidney impairment, and diarrhoea.[2]

This study deals with the removal of nickel ions from aqueous solution. Nickel enters in water sources due to various industrial discharges like battery manufacturing, electroforming, electroplating, alloys, aerospace industries, rubber, plastics, batteries and mining etc.[3] As per the World Health Organization, the permissible nickel concentration in drinking water and wastewaters should not exceed 0.02 mg/L and 900 mg/L[4.]

Though the standard methods like membrane filtration, solvent extraction, ion exchange, reverse osmosis, oxidation, chemical precipitation, etc. are available for the removal of heavy metals from wastewater. However, these techniques suffer from a number of drawbacks, including the production of hazardous chemical sludge, insufficient metal removal, limited efficiency, and a high energy and reagent need.[5] Alternative to these methods, biosorption is a viable, beneficial, and highly recommended because of its many benefits, including its low operation cost, environmental friendliness, minimal or no toxic sludge generation, short operating time, ease of preparation, lack of need for additional nutrients, possibility of metal recovery, and availability.[6]

Papaya, (*Carica papaya*), is a short-lived perennial growing to 30 ft (9.14 m) high, and the economic life of papaya plant is only 3 to 4 years.[7] Though the various parts of papaya plant are used for making medicinal products but its stem is of no use and can be treated as waste. The main or upright growth of banana plant is called a *pseudostem*, which when mature, will obtain a height of 2–8 m. After ripening of bananas, the mother plant dies.. [8] so both the plants after completing their economic life span, their stem pats are considered as dumping waste. In this study papaya and banana plant stem is used for preparation of activated carbon.

II. MATERIALS AND METHODS

2.1 Preparation of adsorbents:

Preparation of PSAC and BSAC: Raw papaya and banana stem were either collected from nearby agricultural field or purchased from local market of Nagpur,(MH). Then these materials were thoroughly washed with tap water to remove dirt and impurities and rinsed several times in DI water and then sun-dried to evaporate the moisture content. After that, dried in an oven for 12 hrs at 70°C. Finally the dried papaya stem was kept at 500°C and banana stem at 300°C in electrical muffle furnace at a rate of 5 °C/min and 150cm^3/min under purified atmospheric nitrogen (98.99%) to make charcoal respectively. Then it was crushed into fine powder to increase surface area and particle size of adsorbents was between 150 and 600um as per IS standard mesh. The sample was washed several time with distilled water to remove chemicals if any and to attain neutral pH (6.5-7.5). the sample was left overnight in an oven at 100°C. Afterward stored in an impermeable vessel for additional use.

<table>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td>Raw papaya stem</td><td>PSAC</td><td>Raw Banana stem</td><td>BSAC</td></tr>
<tr><td colspan="2">Figure 1. Sun dried Papaya stem and its activated carbon</td><td colspan="2">Figure 2. Sun dried Banana stem and its activated carbon</td></tr>
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a. **Adsorption Experiment**:

In the present work, all chemicals were analytical grade and all, stock solutions were prepared with distilled water. The stock solution containing 1000 mg/l of Ni (II) was prepared by dissolving 4.784 g of $NiSO_4.7H_2O$ in 1000 ml of deionized, double distilled water and different adsorbents were used such as Papaya Stem activated carbon (PSAC) and Banana Stem activated carbon(BSAC), Adsorption capacity of PSAC and BSAC for Ni(II) ions was determined by batch studies in a series of 100ml conical flask containing 50 ml of stock solution and their removal efficiency for Nickel were compared. The absorbance was measured by using UV-Spectrophotometer at the maximum absorption wavelength and adsorption capacities were calculated by mass balance equation (1)

$$q_e = \frac{(C0-Ce)V}{m} \text{ -------- --------(1)}$$

where Qe is the concentration of adsorbed heavy metal ions (mg/g), C0 and Ce are the initial and equilibrium metal ion concentration in solution (mg/L), m is the mass of adsorbent (mg), and V is the volume of the adsorbent solution (mL).

The removal percentage (%) of metals from solution were calculated by Equation (2)

$$\% \text{ Removal} = \frac{(C0-Ce)}{Co} \times 100 \text{ ------------ (2)}$$

The Langmuir and Freundlich models employed as empirical isotherm models were expressed as Equations (3) and (4), respectively.

$$q_e = \frac{Qm\ Kl\ Ce}{1+Kl\ Ce} \text{ ------------- (3)}$$

$$q_e = Kf\ Ce^{1/n} \text{ -------------- (4)}$$

where qe and Ce were the same in Equation (1), Qm is the maximum adsorption capacity of adsorbent (mg/g), Kl is the empirical affinity Langmuir coefficient (L/mg), Kf is the Freundlich adsorption affinity coefficient (L/kg), and n is the Freundlich linearity constant, depending on the character of the adsorbent.

Non-linear isotherms were assumed as Langmuir models, as the shape can be expressed by a dimensionless constant separation factor or equilibrium parameter (RL), and R_L is defined as Equation (5)[9]

$$R_L = \frac{1}{1+Kl\ Co} \text{ --------------- (5)}$$

where Kl (L/mg) is Langmuir model constant and C0 (mg/L) is the largest initial concentration of metal solutions. $R_L>1$, $R_L=1$, $0<R_L<1$, $R_L=0$ indicate unfavorable, linear, favorable, and irreversible adsorption, respectively.[10]

III. RESULTS AND DISCUSSION

3.1 Characterisation of Adsorbents-

X-Ray diffraction analysis:

The X-ray diffraction studies were done on XRD analyzer between 10 to 80^o to determine the crystalline phases formed in PSAC and BSAC. The XRD pattern of prepared adsorbents has shown in fig. 3 and fig. 4.

Based on research by Maria de los Angeles [11] having similar XRD pattern, PSAC exhibits a peak at $2\theta = 25.62°$ and 47.17° BSAC exhibits a peak at $2\theta = 24°$ and $2\theta = 43°$ which corresponds to the peak of graphite. At the same time it exhibits noise of powder XRD signals.According to Tchomgui-Kamga(2010) , amorphous materials show better absorbance due to their high surface area and greater number of active sites.[12] In XRD pattern of PSAC and BSAC, there are lesser number of sharp peak and smaller peak height which indicates an amorphous carbonaceous structure, typical of biomass lignicellulosic carbon [13].

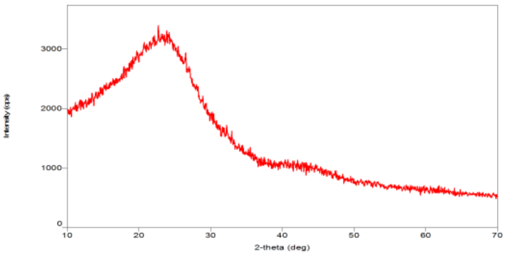

Figure 3. XRD for BSAC

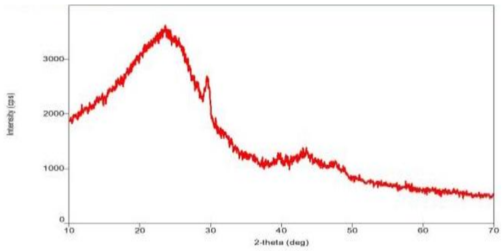

Figure 4. XRD for PSAC

3.2 Effect of pH

pH is one of the most crucial variables in the adsorption of metal ions onto since it affects the surface charge of the adsorbent, the degree of ionisation, and the specification of the adsorbate . Fig. 5 illustrates how pH affects the simultaneous removal of Ni(II) into PSAC and BSAC. Adsorption studies have been conducted for variant pH (4–9) and fixed choice of adsorbent dosage (0.02 g/L), Ni (II) solution concentrations (10 mg/L) and optimized contact time of 120 minutes. These studies indicate that the optimal pH has been about 8. At pH values 4, both metal ions showed low levels of adsorption; however, Between pH values 6.0 and 8.0 the metal sorption increases sharply, attaining maximum values of 91.53 and 92.82 % pH for PSAC and BSAC respectively. Ni(II) removal is reduced at low pH levels because extra H+ ions in the solution compete with Ni(II) ions for active sites. Although the concentration of H+ ions drops as pH is raised, the concentration of Ni(II) ions stays the same, resulting in enhanced absorption.14 When the pH was raised above 8.0, Ni(II) showed a tendency of diminishing sorption, and further increases in sorption were inconsequential since the optimum sorption was obtained at this pH level. This might be explained by Ni(II)'s lower solubility at high pH. Therefore, 8 was chosen as the Ni(II) solution's ideal pH.[15]

3.3 Effect of Contact time

For BSAC and PSAC at a dose of 0.2 g/L at room temperature, metal removal efficiency against contact time, namely 20, 40, 60, 80, and 120 min, was examined. The findings are shown in Fig. 5 and Fig 6. By observing the uptake of the Ni (II) ions over the course of 120 min at room temperature, the impact of contact duration was ascertained. Within 80 minutes, the percentage of metal removed reached its peak; there was then little variation because equilibrium had been gradually reached. The high removal effectiveness during the first 80 minutes may be related to the higher number of initial empty sites at the adsorbent surfaces, which are gradually taken over by metal ions over time [16]. The competition for fewer active sites by metal ions caused the absorption rate to drop as the binding sites became exhausted .[17]

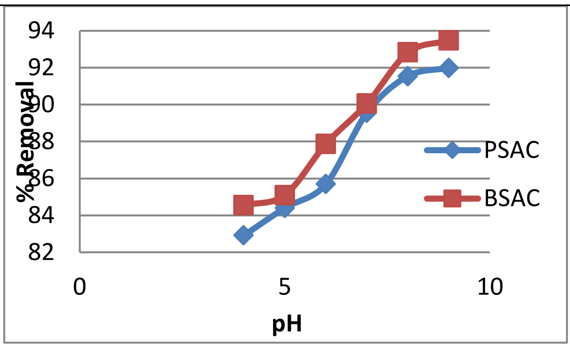

Figure 5. Effect of pH

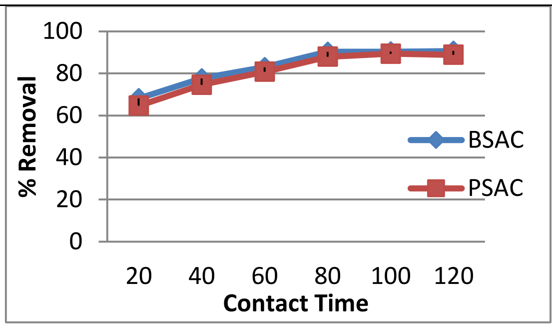

Figure 6. Effect of Contact time

3.4 Determination of Isotherm constants: Langmuir and Freundlich isotherm constants for the adsorption of Ni(II) onto PSAC and BSAC derived adsorbent

Isotherm Constants	for PSAC	for BSAC
Langmuir Isotherm		
q_o (mg/g)	4.673	4.9019
K_L (L/mg)	0.213	0.2441
R^2	0.98	0.9956
R_L	0.319	0.29
Freundlich Isotherm		
K_F (L/mg)	0.894	0.9416
n	1.575	1.573
R^2	0.909	0.9317

IV. CONCLUSION

Utilizing inexpensive activated carbon made from agricultural waste, the removal of Ni(II) ions from aqueous solution by batch adsorption was investigated in the current study. The Langmuir and Freundlich adsorption isotherms and the computed isotherm parameters showed a fair amount of agreement between the experimental results. The amount of nickel ion adsorbed increased as the medium's pH rose.The activated carbon could be used to remove nickel ions from aqueous solutions, according to the dimensionless separation factor (RL). The study offers natural adsorbent that is affordable and effective in removing heavy metal ions from waste water because papaya and banana stem rubbish are both easily accessible and inexpensive..

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