Characterization and Removal of Nickel (II) from Paint Industry Effluent by Rice Husk Adsorbent

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Abstract

Rice husk adsorbent was studied to assess its efficiency in adsorption of nickel from paint industry effluent and to derive vital parameters that would assist in making timely decisions in tertiary treatment of wastewater. Standard methods were used in conducting the experiments. Results showed that significant adsorption of 84.77% of nickel was removed by carbonized rice husk (CRH) in 10 minutes and 98.42% in 60 minutes, a difference of 13.65%. Optimum pH of 8 was observed as 98.91% of nickel was adsorbed. Slight change in the adsorption efficiencies was noticed between 0.2 g and 0.4 g doses of CRH adsorbent, but reasonable and insignificant change occurred between 0.4 g and 1.0 g doses. Langmuir isotherm plot showed that separation factor was 0.998 an indication of favorable adsorption and a good fit for the Langmuir isotherm model. Therefore, the adsorption process was better described by the Langmuir equilibrium isotherm model. Adsorption intensity of 2.02 was observed in the Freundlich model, a value greater than 1.0 an indication of unfavorable adsorption. Lagergren pseudo first- and second-order plots showed that $R^2 = 0.799$ for pseudo first-order and $R^2 = 0.969$ for pseudo second-order reactions, an indication that adsorption of nickel by CRH follow Lagergren second-order kinetic. FTIR spectra identified N-H, O-H, C=H, C=O, C=C-C, C-Cl, P-O-C, and cis-C-H out-of-plane bend stretching bands as the functional groups involved in nickel adsorption by CRH adsorbent. It was concluded that rice husk is a good adsorbent in tertiary treatment of wastewater.

Keywords: Biosorbent, Characterization, Nickel Removal, Paint industry, Rice husk
1. Introduction

Considerable amounts of wastewater, generated from anthropogenic activities such as mining and smelting, fertilizer production, agriculture, and battery manufacturing, pose a high risk to the environment, ecosystems, and human health (Gosar, 2004; Xiao et al., 2017). A variety of treatment methods have been applied to eliminate heavy metals from water, including coagulation (Sancho, 2006), adsorption (Feng et al., 2013), ion exchange (Barakat and Ismat, 2013), electrocoagulation (Kumar et al., 2004), and biological processes (Katsonyannis and Sakakibara, 2011). Of these, adsorption is considered the most cost-effective (Patel and Vashi, 2014) when using sorbents that require little processing, are abundant in nature, or are by-products or waste materials from industry (Devi and Saroha, 2017; Hegazi, 2013; Iakovleva and Silanpaa, 2013).

Solid wastes from mining activities have been assessed as low-cost adsorbents for wastewater purification (Iakovleva and Silanpaa, 2013; Coruh and Ergun, 2011; Feng et al., 2004; Iakovleva et al., 2016; Ozdes et al., 2009; Panda et al., 2011).

A variety of solid wastes have been used for water treatment, including clay-bearing mining waste (Edeltrauda and Rafal, 2012), red mud (Coruh and Ergun, 2011; Hulya et al., 2003; Pepper et al., 2018; Thuy et al., 2016), coal mine-drainage sludge (Hung, 2004), iron ore slime (Panda et al., 2011), and waste mud from copper mines (Ozdes et al., 2009).

Activated carbon (AC) as a common adsorbent has been widely used in various industries such as water and wastewater treatment (Altmann et al., 2015; Islam et al., 2015), as well as in several gas separation and purification processes (Ramos et al., 2010; Lemus et al., 2012). ACs are highly porous, and they present a broad range of pore sizes, from visible cracks to crevices and slits of molecular dimensions.

ACs have been prepared from various raw materials such as sludge, coconut shells, wood char, lignin, petroleum coke, bone char, peat, sawdust, carbon black, rice husk, sugar, peach pits, fish residues, fertilizer waste, waste rubber tire, etc. (Mohan and Pittman, 2006; Al-Qodah and Shawabkah, 2009). ACs have also been produced from waste materials, which are produced from human activities due to the surge of industrialization and urbanization (Hadi et al., 2015). Granular activated carbon (GAC) (Westerhoff et al., 2005; Kim et al., 2010; Islam et al., 2015) and

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powdered activated carbon (PAC) (Yoon et al., 2005; Kim et al., 2010; Altmann et al., 2015) are two forms of ACs, which have been used in adsorption processes.

The adsorption process is usually studied at a given temperature and recognized as an adsorption isotherm. One of them is the Langmuir adsorption isotherm (Langmuir, 1918).

\[ q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \]  

(1)

Where \( q_e \) is amount of metal adsorbed per specific amount of adsorbent (mg/g), \( C_e \) is the equilibrium concentration of the solution (mg/L) and \( Q_0 \) is the maximum amount of metal ions required to form a monolayer (mg/g). The Langmuir equation can be rearranged to a linear form for the convenience of plotting and determination of the Langmuir constant \( (K_L) \) as shown below. The values of \( Q_0 \) and \( K_L \) can be determined from the linear plot of \( 1/q_e \) versus \( 1/C_e \):

\[ \frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \]  

(2)

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and the sorbent using the separation factor or dimensionless equilibrium parameter '\( R_L \)' expressed as in the following equation;

\[ R_L = \frac{1}{1 + K_L C_0} \]  

(3)

Where \( K_L \) is the Langmuir constant and \( C_0 \) is the initial concentration of the metal ion. The value of the separation factor \( R_L \) provides important information about the nature of adsorption. The value of \( R_L \) is between 0 and 1 for favourable adsorption, while \( R_L > 1 \) represents unfavourable adsorption and \( R_L = 1 \) represents linear adsorption. The adsorption process is irreversible if \( R_L = 0 \).

Also we have the Freundlich model given by the expression;

\[ q = K_F C^{1/n} \]  

(4)
Where $K_F$ and $n$ are constants (Weber, Jr., 1972)

The linear form of Freundlich isotherm is expressed as;

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

(5)

Where $1/n$ is the adsorption intensity and is said to be favorable when $0 < 1/n < 1$

and the Brunauer-Emmitt-Teller (BET) model expressed as;

$$\frac{c}{(c_s-c)q} = \left(\frac{K_B-1}{K_Bq_{n}}\right)\frac{c}{c_s} + \frac{1}{K_Bq_{n}}$$

(6)

Where $c_s$ and $K_B$ are the solute concentrations when all layers are saturated and energy of adsorption is constant.

Indiscriminate disposal of rice husk into the environment from Eha-Amufu rice mill usually create a lot of problem in this community that it becomes necessary to subject this waste to useful resource by using it to treat wastewater contaminated with Ni(II). People from Onitsha metropolis in Anambra state of Nigeria and its environs experience nausea, vomiting, vertigo, irritation, acute respiratory distress syndrome etc. which are symptoms of acute nickel toxicity. They source their water for treatment and consumption from Nkisi stream where D'Amicable Paint Company in Onitsha dispose their wastewater. However, water-soluble nickel compounds are more toxic than the less soluble compounds which is likely the cause of acute nickel toxicity experienced by this community. Findings from this research will assist water management board in making timely decisions on how to manage water supply in this locality and mitigate diseases spread linked to nickel toxicity.

2. Materials and Methods

2.1. Samples and Sampling Techniques

The rice husks (RH) sample was collected from Eha-Amufu rice mill in Enugu state, while the wastewater effluent was sourced from D'Amicable Paint Company in Onitsha in Anambra state both in Nigeria. The adsorbent used in this study was derived from rice husks. The rice husks were
reduced to smaller sizes, screened, washed and de-ionized with water to remove dirt, subsequently
dried in the oven in GALLENKAMP hot box oven with fan (Model: Size 2 CHF097 XX2.5) in
accordance with BS 1377 (1975) at 105 °C for 5 hours to remove moisture. The dried adsorbents
were ground and samples passing sieve mesh 150 μm were selected for adsorption studies

2.1.1. Carbonization

Carbonization of the sample was carried out in a muffle furnace model KGYV BUDAPEST
KCC086/50-120. 3phases. The rice husks was carbonized at 500°C for two hours and was held at
this temperature for 60 minutes, after which the charred products were allowed to cool to room
temperature before use.

2.1.2. Preparation of 60% Phosphoric Acid (H₃PO₄) used for Activation.

10 g sample of H₃PO₄ pellets was weighed using Citizen® electronic balance, model MP-5000A
with 1.0 g accuracy and was dissolved in 100 ml distilled water in a measuring cylinder.
Subsequently, 40 ml of the dissolved sample was measured and stored in an air-tight container.
The remaining 60 ml of the H₃PO₄ was diluted up to 1000 ml of H₃PO₄ solution with distilled
water resulting in 60% solution of H₃PO₄ required.

2.1.3. Preparation of Activated Carbon

300 g sample of the charred carbonized RH was weighed using Citizen® electronic balance, model
MP-5000A and impregnated in the 60% acidic solution of H₃PO₄ in a beaker. The mixture was
thoroughly stirred with a glass rod in order to obtain a homogeneous solution and left for 24 hours
for proper impregnation. After 24 hours, the mixture was washed with distilled water repeatedly
until pH of the water used for washing gave a value near neutral and the sample was dried in an
oven at a temperature of 105°C for 1 hour and stored in an air-tight container.

2.1.4. Paint Effluent Characterization

The paint effluent from D'Amicable Paint Company was analyzed for the presence of heavy
metals such as nickel, vanadium, zinc, lead, manganese and chromium by digesting 100 ml of the
effluent by using 10 ml triple acid mixture (5:1:1 - HNO₃ : HClO₄ : H₂SO₄) in a 250 ml conical
flask placed in a fumed cupboard. The sample was properly covered with aluminum foil to avoid
spillage and heated on a hot plate until the solution was reduced to 10 ml volume. It was later allowed to cool and was made up to 40 ml with distilled water before it was filtered into a 50 ml standard flask ready for further analysis. Concentrations of heavy metals in the wastewater was measured using Atomic Absorption Spectrophotometer (Model: UNICO 1100).

2.2. Experimental Procedures

The initial pH of the paint effluent sample was taken as 6.47 using model (pH-2601) pH meter. The effluent was poured into beakers and was adjusted to pH from 2 to 10 as required. Various doses of carbonized rice husk (CRH) at 0.2 g intervals from 0.2 to 1.0 g were weighed using Citizen® electronic balance, model MP-5000A and introduced into plastic bottles. The experimental procedure is a long and painstaking process which involved the use of Design Experts, Buckscientific USA Model 201 VGP (Id: Ni, Lot Name: 125, N. Samples: 125, Checksum: 21632362 Data integrity verified). One-Factor-At-A-Time (OFAT) experimental approach was used in this study. This involves keeping the pH and dosage constant and varying the contact times from 10 minutes to 60 minutes with the exclusion of 50 minutes. Next, still keeping the pH constant, vary the dosages and contact times (e.g. pH = 2, dosage = 0.2g, contact times = 10, 20, 30, 40, 60 minutes; pH = 2, dosage = 0.4 g, contact times = 10, 20, 30, 40, 60 minutes ........ pH = 10, dosage = 1, contact times = 10, 20, 30, 40, 60 minutes) all giving a total of 125 test samples. These samples were placed in a speed adjusting multipurpose vibrator model HY-2 at room temperature (301±1 K) and with sporadic agitation for 7 days and rotational speed of 100 rpm. Variation of pH between 2 to 10 was done by using 0.1 M solution of HCl and 0.1 M NaOH for adjustments. For each of the parameter studied, the solid phase was separated using Whitman filter paper No. 1 and the residual metal concentrations present in the supernatant was determined using the Atomic Absorption Spectrophotometer (Model: UNICO 1100). The amount of metal ion adsorbed onto activated carbon at any time, \( q_t \) is given as:

\[
Q = \frac{(c_a - c_e)V}{m} \quad (7)
\]

Where \( Q \) represents the adsorbed amount, \( c_a \) the initial concentration, \( c_e \) the equilibrium concentration, \( V \) the total volume of solution, and \( m \) the mass of activated carbon employed (Bernal et al., 2018). But for (Nguyen et al., 2019), the amount of adsorbate that was adsorbed at
equilibrium, $q_e$ (mg/g), or at time $t$, $q_t$ (mg/g), will be calculated by the following mass balance Equations (5) and (6);

$$q_e = \frac{(C_0 - C_e)V}{m}$$  \hspace{1cm} (8)

$$q_t = \frac{(C_0 - C_t)V}{m}$$  \hspace{1cm} (9)

Where $C_0$ (mg/L), $C_e$ (mg/L), $C_t$ (mg/L) are the adsorbate concentrations at beginning, equilibrium and time respectively; $m$ (g) is the mass of used adsorbent; and $V$ (L) presents the volume of the adsorbate solution.

In this study, the factors considered are contact time ($x_1$), pH ($x_2$) and dosage ($x_3$) so that we have the case of $5k$ factorial design which involves $k$ factors each at 3 levels thus, making a $5^3$ design experiment. Design Experts was used to determine the number of runs in the experiment, and the runs corresponding to significant sorption in each of the factors considered was used as criteria for selecting relevant data prior to analysis.

3. Results and Discussion

Table 1 presents the concentrations of the contaminants found in the paint effluent from D'Amicable Paint Company at Onitsha in Anambra state of Nigeria before adsorption. These results were obtained using the Atomic Absorption Spectrophotometer (Model: UNICO 1100). These variables were compared with the World Health Organization (WHO), European Union (EU), Canada, USA and Russia Standards and it was observed that only pH of the water that satisfy these standards, an indication of a highly polluted water based on the concentrations of the contaminants in the paint effluent.
Table 1: Concentrations of water quality variables in paint effluent before adsorption

<table>
<thead>
<tr>
<th>Variable</th>
<th>TDS</th>
<th>Cr</th>
<th>Mn</th>
<th>Zn</th>
<th>Ni</th>
<th>pH</th>
<th>BOD</th>
<th>Cl</th>
<th>NO3</th>
<th>PO4</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standards</strong></td>
<td><strong>Concentrations (mg/l)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laboratory Results</td>
<td>5668.9</td>
<td>3.85</td>
<td>42790</td>
<td>1782</td>
<td>250</td>
<td>6.5</td>
<td>543.0</td>
<td>60.27</td>
<td>325</td>
<td>12.5</td>
<td>29.4</td>
</tr>
<tr>
<td>WHO</td>
<td>1000</td>
<td>0.05</td>
<td>0.5</td>
<td>3</td>
<td>0.02</td>
<td>&lt; 8</td>
<td>_</td>
<td>_</td>
<td>250</td>
<td>50</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>EU</strong></td>
<td>0.05</td>
<td>0.05</td>
<td>0.1-5.0</td>
<td>0.05</td>
<td>6.5-8.5</td>
<td>_</td>
<td>25</td>
<td>50</td>
<td>5.0</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Drinking Water</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Canada</strong></td>
<td>0.05</td>
<td>0.05</td>
<td>5.0</td>
<td>_</td>
<td>6.5-8.5</td>
<td>_</td>
<td>250</td>
<td>_</td>
<td>_</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td><strong>USA</strong></td>
<td>0.05</td>
<td>0.05</td>
<td>5.0</td>
<td>_</td>
<td>6.5-8.5</td>
<td>_</td>
<td>250</td>
<td>_</td>
<td>_</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>Russia</td>
<td>1000</td>
<td>0.03</td>
<td>0.5</td>
<td>5.0</td>
<td>0.02</td>
<td>6.0-9.0</td>
<td>3.0</td>
<td>350</td>
<td>45</td>
<td>_</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Fisheries and aquatic life</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>EU</strong></td>
<td>25</td>
<td>_</td>
<td>_</td>
<td>_</td>
<td>0.03-2.0</td>
<td>6.0-9.0</td>
<td>3.0-6.0</td>
<td>_</td>
<td>_</td>
<td>_</td>
<td></td>
</tr>
<tr>
<td><strong>Canada</strong></td>
<td>_</td>
<td>0.02-0.002</td>
<td>_</td>
<td>0.03</td>
<td>0.025-0.15</td>
<td>6.5-9.0</td>
<td>_</td>
<td>_</td>
<td>_</td>
<td>0.001-0.007</td>
<td></td>
</tr>
<tr>
<td>Russia</td>
<td>_</td>
<td>0.02-0.005</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>_</td>
<td>3.0</td>
<td>300</td>
<td>40</td>
<td>_</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Sources: Laboratory work, 2020; Environment Canada, 1987; CEC, 1978; CEC, 1980; Committee of Fisheries, 1993; Gray, 1994; WHO, 1993

Figure 1: Variation of adsorption efficiency with time

Figure 2: Variation of adsorption efficiency with pH

Figure 1 presented the relationship between adsorption efficiency with time. Results indicated that significant sorption took place within the first 10 minutes as 84.77% of nickel was adsorbed while 92.55% of nickel was adsorbed in 20 minutes, which is 7.78% difference and no optimal time was reached. Marvette and Abdel-Moneim (2014) reported similar result and Brahmaiah et al. (2015a)
reported optimum time of 40 minutes for 56% adsorption and 50 minutes for 82% adsorption of nickel for untreated and treated rice husk. The entire trend showed remarkable decrease in sorption capacity with time after optimum as shown in Figures 3(a) - (h) which showed the morphology and textural examination of the adsorbent. The scanning electron microscopy (SEM) micrograph of carbonized rice husk adsorbent (RHA) for control, Figure 3(a) (i.e. before adsorption started taking place on the surface of the RHA), at 10, 20, 30, 40, 45, 50 and 60 minutes corresponding to Figures 3(b), 3(c), 3(d), 3(e), 3(f), 3(g) and 3(h). These SEM micrograph showed the decreasing porosity of the adsorbent with time, an indication that as sorption takes place the adsorption sites of the adsorbent becomes more clogged giving rise to decrease in sorption with time due to saturation. It is easily seen that between Figures 3(a) and 3(b), the pores are large enough which is instrumental to the 84.77% sorption, while between Figures 3(b) and 3(c) the pores have significantly clogged which is the reason for only 7.78% increase in sorption between 10 to 20 minutes. Figures 3(d) to 3(h) are evidence of the remarkable decrease in sorption of nickel by RHA adsorbent as seen Figure 1 because 92.55%, 93.22%, 95.80% and 98.42% of nickel was sorbed at 20, 30, 40 and 60 minutes respectively.

Figures 3(a) - (h): Scanning electron microscopy (SEM) micrograph showing the stages of sorption of nickel by carbonized rice husk (CRH) adsorbent.

Figure 2 showed variation of pH with adsorption capacity. Results indicated that optimum pH was 8 because at that point 98.91% of nickel was adsorbed. Per cent sorption of nickel was 93.37%, 93.73%, 94.37% and 96.84% at pH of 2, 3, 6 and 10 respectively. Nevertheless, optimum pH of 4 was reported by (Rodriguez et al., 2010; Sobhanardakarni and Zandipak, 2015), while Spurthi et
al. (2015) and Marvette and Abdel-Moneim (2014) reported optimum pH of 6 for adsorption of nickel by rice husk adsorbent.

![Figure 4: Variation of adsorption efficiency with dosage](image)

Figure 4 show the effect of dosage on adsorption efficiency. There was no significant difference in adsorption efficiency between 0.2 g and 0.4 g doses. Reasonable difference were observed from 0.4 g to 1.0 g doses though the optimum dose was not attained as observed in the relationship between pH and adsorption efficiency. However, a linear relationship exist between dosage and adsorption efficiency since sorption increases with dosage. Spurthi et al. (2015) reported optimum dosage of 12g/100ml and 8g/100ml sample of treated and untreated rice husk respectively.

Table 5: Langmuir and Freundlich isotherms for adsorption of nickel (II) by rice husk biosorbent

<table>
<thead>
<tr>
<th>Dosage (g)</th>
<th>$C_e$ (mg/l)</th>
<th>$q_e$ (mg/l)</th>
<th>$1/C_e$</th>
<th>$1/q_e$</th>
<th>$\ln C_e$</th>
<th>$\ln q_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>3.962</td>
<td>192.690</td>
<td>0.252</td>
<td>0.005</td>
<td>1.377</td>
<td>5.261</td>
</tr>
<tr>
<td>0.4</td>
<td>3.207</td>
<td>98.233</td>
<td>0.312</td>
<td>0.010</td>
<td>1.165</td>
<td>4.587</td>
</tr>
<tr>
<td>0.6</td>
<td>2.416</td>
<td>66.807</td>
<td>0.414</td>
<td>0.015</td>
<td>0.882</td>
<td>4.202</td>
</tr>
<tr>
<td>0.8</td>
<td>1.941</td>
<td>50.699</td>
<td>0.515</td>
<td>0.020</td>
<td>0.663</td>
<td>3.926</td>
</tr>
<tr>
<td>1.0</td>
<td>1.081</td>
<td>41.419</td>
<td>0.925</td>
<td>0.024</td>
<td>0.078</td>
<td>3.724</td>
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</table>

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Figure 4: Langmuir isotherm plot for adsorption of nickel (II) by rice husk biosorbent

Figure 5: Freundlich isotherm plot for adsorption of nickel (II) by rice husk biosorbent

From figure 4, \(1/Q_0 = 0.002\), \(Q_0 = 500\), \(Q_0K_L = 0.025\), \(K_L = 0.00005\) for concentration \(Q_0\) of 500 mg/l, so that \(R_L = 0.998\). The value of \(R_L\) gives important information about adsorption, which is \((0 < R_L < 1)\) for favorable adsorption, \((R_L = 0)\) for irreversible adsorption, \((R_L = 1)\) for linear adsorption and \((R_L > 1)\) for unfavorable adsorption. In this case \((R_L = 0.976)\) and \((R^2 = 0.814)\) indicate that the adsorption process is favorable and have a very good fit for Langmuir isotherm. In figure 5, the adsorption intensity \(1/n\) was 2.02 which is greater 1, an indication of unfavorable adsorption since \((0 < 1/n < 1)\) is for favorable adsorption (Ahmad Farhan, 2016) even though the Freundlich model showed a better fit with \(R^2 = 0.972\) against \(R^2 = 0.814\) for the Langmuir model. An \(R_L = 0.152\), \(R_L = 0.285\) and \(R^2 = 0.994\), \(R^2 = 0.928\) was obtained by (Rodriguez et al., 2010) for untreated and treated rice husk respectively. Therefore, the adsorption process was better described by the Langmuir equilibrium isotherm model.

Table 6: Lagergren pseudo first- and second-order rate constants for adsorption of Ni(II) by carbonated rice husk adsorbent

<table>
<thead>
<tr>
<th>Time (Mins)</th>
<th>(q_e)</th>
<th>(q_t)</th>
<th>(q_e - q_t)</th>
<th>(ln(q_e - q_t))</th>
<th>(t/q_t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>22.660</td>
<td>4.037</td>
<td>18.623</td>
<td>2.924</td>
<td>2.477</td>
</tr>
<tr>
<td>20</td>
<td>40.876</td>
<td>3.762</td>
<td>37.114</td>
<td>3.614</td>
<td>5.316</td>
</tr>
<tr>
<td>30</td>
<td>73.065</td>
<td>3.205</td>
<td>69.860</td>
<td>4.246</td>
<td>9.360</td>
</tr>
<tr>
<td>40</td>
<td>88.217</td>
<td>2.022</td>
<td>86.195</td>
<td>4.457</td>
<td>19.780</td>
</tr>
<tr>
<td>60</td>
<td>97.790</td>
<td>1.941</td>
<td>95.849</td>
<td>4.563</td>
<td>30.912</td>
</tr>
</tbody>
</table>

\(y = 0.0257x + 0.0024\)
\(R^2 = 0.8145\)

\(y = 2.0202x + 3.11\)
\(R^2 = 0.9727\)

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Figures 6 and 7 are plots of the Lagergren pseudo first- and second-order equations for the experimental data. Correlation coefficient $R^2 = 0.799$ for pseudo first-order kinetic and $R^2 = 0.969$ for pseudo second-order kinetic. These results showed that pseudo second-order equation fitted the experimental data well with a correlation coefficient ($R^2$) nearly close to unity. Kowanga et al. (2016) found $k_1 = 0.0506$, $R^2 = 0.985$ for untreated rice husk, $k_1 = -0.0207$, $R^2 = 0.990$ for treated rice husk and $k_2 = 0.0160$, $R^2 = 0.988$ for untreated rice husk and $k_2 = 0.0326$, $R^2 = 0.979$ for treated rice husk respectively. These results agree with the findings in this research.
Figure 8: FTIR spectrum analysis of CRH adsorbent before adsorption of nickel (II)

In figure 8, the FTIR spectrum of the adsorbent show characteristic peaks in the plot of transmittance as a function of wave number. The broad band 3276.3 cm\(^{-1}\) is assigned to the Amine (N-H) group of medium intensity. Wave number 2926.0 cm\(^{-1}\) fall in the carboxylic acid (O-H) stretch usually associated with strong and broad intensity. However, there was a shift within this group from wave number 2926.0 cm\(^{-1}\) to 2855.1 cm\(^{-1}\) during Ni (II) adsorption. Wave number 2165.6 cm\(^{-1}\) is evidence of sorption of the alkene group (C=H) stretch of medium intensity, with a shift within this group which occurred from 2165.6 cm\(^{-1}\) to 2109.7 cm\(^{-1}\) bands respectively. Broad band 1707.1 cm\(^{-1}\) indicate the presence of ketone (C=O) and carboxylic acid (O-H) stretches.

Wavenumbers 1580.4 cm\(^{-1}\), 1379.1 cm\(^{-1}\), 790.2 cm\(^{-1}\), 1047.4 cm\(^{-1}\), and 700.7 cm\(^{-1}\), evidenced the presence and sorption of aromatic ring (C=C-C), organic sulfate, alkyl halide (C-Cl), epoxy and oxirane rings, aliphatic phosphates (P-O-C) and the cis-C-H out-of-plane bend stretches respectively. The change in the transmittance in the FTIR spectra for metal loaded biomass of CRH showed that the above functional groups were adsorbed by nickel (II) during the reactions. The bands are indications of interaction of these functional groups on the surface of rice husk adsorbent. The results above agree with the work of Ahmady-Asbchin et al. (2018).

Figure 9: FTIR spectrum analysis of CRH adsorbent after adsorption of nickel (II)

The FTIR spectrum presented in Figure 9 is the variation of transmittance with wave bands after adsorption of Ni(II). The diagram showed that many peaks disappeared, while few peaks shifted.
The disappearance are indications of nonexistence of these functional groups in the reaction system signifying complete adsorption by the adsorbent. There appeared a shift in amino (N-H) compounds stretch from band 3276.3 cm\(^{-1}\) to 3332.2 cm\(^{-1}\). New peak of broad band 2881.2 cm\(^{-1}\) appeared which is absorption band for long-chain linear aliphatic or carboxylic acid (O-H) compounds, and occurred as a result of some unknown reactions going on in the system.

Other broad bands introduced are 1606.5 cm\(^{-1}\) and 1408.9 cm\(^{-1}\), evidencing the presence of carbonyl (C=O) compounds and ammonium ion stretches. There is presence of the broad band 790.2 cm\(^{-1}\) both before and after adsorption. This evidenced the conservative nature of alkyl halide (C-Cl) compounds to adsorption by the adsorbents. And finally, an insignificant shift of the broad band 1407.4 cm\(^{-1}\) to 1043.7 cm\(^{-1}\) indicating insignificant removal of this functional group by the adsorbent.

4. Conclusion

This paper presents the outcomes from characterization and removal Nickel (II) from paint industry effluent by rice husk adsorbent. Results showed that significant adsorption of 98.42% of nickel was removed by carbonized rice husk (CRH) in 60 minutes. Langmuir isotherm plot showed that separation factor was 0.998 an indication of favorable adsorption. Lagergren pseudo first- and second-order plots showed that \(R^2 = 0.799\) for pseudo first-order and \(R^2 = 0.969\) for pseudo second-order reactions, an inference that adsorption of nickel by CRH follow Lagergren second-order kinetic. These results evident that rice husk is an excellent adsorbent for contaminant removal from wastewaters.

References


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