SYNERGISTIC STUDIES ON THE REMOVAL OF Ni^{2+} AND Pb^{2+} FROM AQUEOUS SOLUTIONS USING CHITOSAN AND GRANULAR ACTIVATED CHARCOAL: EQUILIBRIUM CONSIDERATION

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ABSTRACT
This study compares the potential of three adsorbents, chitosan, activated charcoal and a combination of both (composite adsorbent) in removing Ni(II) and Pb(II) ions from aqueous solutions in a batch equilibrium studies. The influences of pH and concentration on the adsorption process were examined. The Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were employed to assess the equilibrium experimental data and the correlation coefficients obtained show that Langmuir provided the best description for adsorption of Ni(II) and Pb(II) ions onto chitosan, Freundlich gave best interpretation to adsorption of the metal ions onto activated charcoal while adsorption of the metal ions onto the composite adsorbent was best fitted by the Dubinin-Radushkevich isotherm. Maximum adsorption capacity corresponding to monolayer coverage (q_{max} values in mg/g) obtained from Langmuir plots are 55.25 and 49.26 respectively for Pb(II) and Ni(II) adsorption onto chitosan, 70.42 and 50.51 for adsorption onto activated charcoal and 125 and 67.57 onto the composite adsorbent. Assessment of the maximum amount of metal ion adsorbed onto the three adsorbents showed that Pb(II) ions were better adsorbed than Ni(II) ions. The affinity of the adsorbents for the metal ions also follows the trend: composite adsorbent > granular activated charcoal > chitosan, indicating that the combination of the two adsorbents provided a great synergistic effect leading to enhanced removal of the metal ions from aqueous solutions. The adsorption process was found to be pH-dependent and the results indicate that the optimum pH for adsorption of Pb(II) and Ni(II) onto chitosan and the activated charcoal occurred at 6.0 having maximum removal efficiencies of 98.57% and 97.79% respectively for Pb(II) and Ni(II) ions onto chitosan and 99.11% and 98.73% for their adsorption onto activated charcoal following the initial order. That of the composite adsorbent displays a different pH dependence with maximum adsorption of Pb(II) occurring at pH 4.0 with maximum removal efficiency of 99.89% and Ni(II) at 6.0 with removal efficiency of 99.60 %.

Keywords: Activated charcoal, biosorption, chitosan, composite adsorbent, Isotherms.
INTRODUCTION
The problems of the ecosystem are increasing with developing technology. Heavy metal pollution is one of the main problems affecting our ecosystem. Toxic metal compounds coming to the earth's surface not only reach the earth's waters (seas, lakes, ponds and reservoirs), but also contaminate underground water in trace amounts by leaking through the soil after rain and snow. Therefore, the earth's waters contain various toxic metals. Heavy metal contamination of water sources is of great concern because of its non-biodegradability and toxic effect to humans, other animals and plants in our environment, even at very low concentrations. The main sources of heavy metal contamination come from various industrial activities, such as mining operations, metal smelting and plating, electric device manufacturing, power plants, waste incinerators, battery manufacturing, domestic effluents, agricultural run-off and so on. Many of the heavy metals, including cadmium, lead, mercury, copper etc. have been included in the U.S. Environmental Protection Agency's priority list of pollutants. The effects of heavy metals in water and wastewater range from beneficial to toxic, depending on their concentration. Since heavy metal ions are not biodegradable in nature, effective removal of heavy metal ions from aqueous solutions and waste effluents through various technologies (physical or chemical) is important in the protection of environment and public health. Various chemical and physical methods have been used to remove metal ions from solutions in the past few decades. These methods include: chemical precipitation, solvent extraction, ion exchange, evaporation, reverse osmosis, electrolysis and adsorption. Among these methods, chemical precipitation, solvent extraction, ion exchange and adsorption are more commonly used. Chemical precipitation has traditionally been used to remove heavy metal ions from waste water with relatively high concentrations. The operation of chemical precipitation is simple but generates large quantities of sludge that require further disposal. In addition, chemical precipitation is usually not effective to remove trace levels of metal ions from aqueous solutions. Solvent extraction has widely been used in organometallic removal. Although the process may have fast kinetics and high capacity, solvent extraction is often costly due to the quantity and specific type of solvents needed. Ion exchange method has commonly been used to remove metal ions from water or wastewater, but the process has slow kinetics, consumes large quantity of chemicals, generates hazardous streams and is not well applied to heavy metal ions due to possible problem of resin pollution. Adsorption has been considered as, possibly, the most cost-effective method for heavy metal ion removal, especially at medium to low concentrations, because the process is simple and chemical consumption or waste generation is not a significant issue. However traditional adsorbents, such as activated carbon are often not very effective to adsorb heavy metals from water or wastewater and are also expensive. For the removal of heavy metals from wastewater, it is important to have effective and cheap adsorbents available for large scale treatment applications. In recent years, biosorption using materials of biological origin has emerged as an attractive method for the removal of heavy metal ions from aqueous solutions, largely due to the unique properties of these materials being environmentally benign, low cost, effective in trace metal level and easy to regenerate for reuse. In the present study, three adsorbents, chitosan, granular activated charcoal and a combination of both adsorbents (composite adsorbent) were compared for their efficiency in removing Pb(II) and Ni(II) ions from aqueous solutions. The effects of pH and concentration were tested and the amount adsorbed as well as the mechanism of the process was assessed using different equilibrium isotherm models.

MATERIALS AND METHODS
Preparation of metal ion concentrations
All the reagents used were of analytical reagent grade and were used without further purification. No activation of the adsorbents was done since they were commercially prepared. Distilled and deionized water was used in the preparation of all sample solutions. 1000 mg/L solutions of lead and nickel were prepared as stock solutions from their salts Pb(NO$_3$)$_2$ and NiSO$_4$.6H$_2$O respectively. From the stock solutions, various concentrations ranging from 10 mg/L to 100 mg/L used for the adsorption study was prepared by serial dilution of the stock solutions.

Batch Adsorption Experiments
The effect of concentration on equilibrium adsorption of Pb$^{2+}$ and Ni$^{2+}$ onto chitosan powder, granular activated animal charcoal and
the composite (mixture of the two) adsorbent was carried out by introducing 50 cm$^3$ of various concentrations of Pb(II) and Ni(II) ions into 250 mL conical flasks and then adding 0.5 g of each of the adsorbents at a temperature of 30°C and pH 4.5. The flasks were shaken for 180 min on a rotary shaker and at the end of the contact time (3 h), the mixtures were filtered rapidly into separate sample bottles. The residual metal ion concentration in the filtrate was determined using UNICAM (solar AAS 969) atomic absorption spectrophotometer.

The effect of pH on the adsorption process was also carried out by introducing 50 cm$^3$ of 100 mg/L of Pb$^{2+}$ and Ni$^{2+}$ into different 250 mL conical flasks containing 0.5 g of each of the adsorbents and then adjusting the pH of the solutions from pH 2 to 10 using either 0.1 M HCl or 0.1 M NaOH solution and at a fixed temperature of 30°C. The flasks were agitated for 3 h and then filtered rapidly. The residual metal ion concentration in the filtrate was finally determined using UNICAM (solar AAS 969) atomic absorption spectrophotometer. The amount of the metal ions adsorbed was calculated by difference. The analysis was carried out in triplicates and mean residual concentrations analyzed. The amount of metal ions adsorbed at equilibrium, $q_e$ (mg/g) was determined using the mass balance equation (1).

$$q_e = \frac{C_0 - C_e}{m} \times V$$

where $C_0$ and $C_e$ are the initial and equilibrium concentrations (mg/L), $V$ is the volume of solution (L) and $m$ the dry mass of the adsorbents (g).

RESULTS AND DISCUSSION

Effect of pH on the adsorption of the metal ions

The amounts of Pb(II) and Ni(II) adsorbed as a function of initial pH are shown in Figs. 1 – 3. The pH of an aqueous solution is an important factor that affects both the availability of metal ions in solution and the number of binding sites on the adsorbent$^{13,14}$. This means that the dependence of metal adsorption on pH is linked to both the metal chemistry in solution and the ionization state of the functional groups of the adsorbent. The range of pH values 2.0 to 8.0 selected in our study were chosen to avoid the precipitation of Pb(II) and Ni(II) ions in solution at higher pH. Results show that the amount of metal ions adsorbed from the solutions by the adsorbents increased as the pH of the metal ion solutions increased from pH 2.0 to pH 6.0 and then decreased as the pH is increased above 6.0. At low pH, the protons compete with the metal ions for the binding sites on the adsorbent surface leading to a reduction in the amount of metal ions adsorbed as a result of electrostatic repulsion. Also, at higher pH, the proton concentrations decrease thereby creating more binding sites on the adsorbents, consequently leading to enhanced metal uptake. From Figs. 1 - 3, it is observed that the adsorption of Pb$^{2+}$ and Ni$^{2+}$ onto the granular activated charcoal and chitosan depends on pH and maximum adsorption occurred at pH 6.0 for both ions. The adsorption of the Pb(II) and Ni(II) ions onto the composite adsorbent displayed a slightly different pH dependence having the optimum pH for Pb(II) at pH 4.0 and that of Ni(II) at pH 6.0. Also, the increase in amount of Ni(II) adsorbed onto the composite adsorbent further increased at the pH 8. This increase could have resulted from precipitation of the metal ions as an insoluble Nickel (II) hydroxide at the higher pH 8. The adsorbents generally show higher affinity for Pb$^{2+}$ than for Ni$^{2+}$ at the initial concentration of 100 mg L$^{-1}$ used.

Fig. 1: Amount of metal ions adsorbed onto chitosan at different initial pH
Effect of metal ion concentration
The effects of initial metal ion concentration on the percentage of Pb$^{2+}$ and Ni$^{2+}$ adsorbed are shown in Figures 4 – 6. From Figures 4 - 6, it can be observed that with increase in metal ion concentrations from 10 mg/L to 100 mg/L, the removal efficiency of chitosan decreased from 98.80% and 98.30% to 98.57% and 97.90% for Pb$^{2+}$ and Ni$^{2+}$ adsorption respectively, while that of activated charcoal decreased from 99.15 % and 98.99 % to 99.03 % and 98.70 % respectively for Pb$^{2+}$ and Ni$^{2+}$. A similar decrease in removal efficiency was also observed for adsorption onto the composite adsorbent. For the composite adsorbent (chitosan + activated charcoal), Pb$^{2+}$ decreased from 99.88% to 99.87% while Ni$^{2+}$ decreased from 99.57% to 99.51%. This is a fact because adsorption sites are unsaturated at lower metal ion concentration. However, at higher concentrations, the adsorption sites become saturated, leading to decrease in the adsorption efficiency of the adsorbents for the metal ions. A similar observation had been made by Imamoglu and Tekir in their study on the removal of copper(II) and lead(II) ions from aqueous solutions by adsorption onto activated carbon from a new precursor hazelnut husks. Therefore, at lower metal ion concentrations, almost all the ions are adsorbed whereas at higher initial concentrations, the ratio of initial amount of the metal ions to the available surface area is high; hence fractional adsorption becomes dependent on initial concentration. In this study, the 0.5 g L$^{-1}$ adsorbent dose selected may have contained enough exchangeable sites at lower concentrations of the metal ions, but as the initial concentrations increase to 100 mg L$^{-1}$,
the exchangeable sites in the 0.5 g of the adsorbent will not be enough to cover this concentration so that decrease in percentage removal becomes obvious. Results generally showed that there was greater removal of Pb$^{2+}$ than Ni$^{2+}$ from the solutions. It was also observed that the composite adsorbent showed an enhanced removal for the metal ions as compared to activated carbon and chitosan. The affinity of adsorbents for the Pb(II) and Ni(II) ions follows the trend: composite adsorbent > activated charcoal > chitosan, indicating that the combination of the two adsorbents (composite adsorbent) provided a great synergistic effect that lead to enhanced removal of the metal ions from aqueous solutions.

Fig. 4: Plot of percentage metal ions adsorbed vs initial conc. for adsorption of the metal ions onto chitosan

Fig. 5: Plot of percentage metal ions adsorbed vs initial conc. for adsorption of the metal ions onto the activated charcoal

Fig. 6: Plot of percentage metal ions adsorbed vs initial conc. for adsorption of the metal ions onto the composite adsorbent
ADSORPTION ISOTHERMS

Adsorption isotherm is established when the concentration of an adsorbate (metal ion) in a bulk solution (C_e) is in dynamic balance with that at the interface. The metal ion uptake capacities in the present study were evaluated using the Langmuir, Freundlich and Dubinin – Radushkevich isotherm models.

Langmuir Isotherm Model

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The isotherm is mainly based on the monolayer adsorption on the active reaction sites of the adsorbent and is generally expressed as:\[ \frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_L} + \frac{C_e}{q_{\text{max}}} \] \hspace{1cm} (1)

where \(q_e\) is the equilibrium adsorption uptake of heavy metal ions, \(q_{\text{max}}\) is the maximum adsorption capacity corresponding to the complete monolayer coverage and \(K_L\) is the Langmuir constant which is related to the energy of adsorption. The linear plots of \(C_e/q_e\) vs \(C_e\) as depicted in Figures 7 - 9 showed that the adsorption study follows the Langmuir adsorption isotherm model. The adsorption of the metal ions onto chitosan was best described by the Langmuir model indicating that the adsorption process may have proceeded through a monolayer coverage. The Langmuir constants, \(q_{\text{max}}\) and \(K_L\) for the three adsorbents were evaluated from the slope and intercept of the linear Langmuir plots and are presented in Table 1. The \(q_{\text{max}}\) values are used to compare the efficiencies of the adsorbents in our study (chitosan, activated charcoal and the composite) with other adsorbents, which have been applied for the removal of the same metal ions from aqueous solutions. The \(q_{\text{max}}\) values obtained from this study indicate better removal for Pb^{2+} than Ni^{2+} and that the composite adsorbent displayed higher removal efficiency for the metal ions as compared to the chitosan and activated charcoal. This result shows that the combination of the two adsorbents (chitosan and charcoal) may have produced a strong synergistic effect leading to enhanced uptake of the metals ions from aqueous solutions. Also, the values of the linear regression coefficient \((R^2)\) displayed in Table 1 are all greater than 0.950, suggesting a good fitting of the experimental data into the Langmuir isotherm equation.

The essential characteristics of the Langmuir isotherm is expressed in terms of a dimensionless constant termed separation factor or equilibrium parameter, \(R_L\), which is used to predict whether an adsorption system is “favorable” or “unfavorable”. The separation factor, \(R_L\) is defined as:\[ R_L = \frac{1}{(1 + K_L C_m)} \] \hspace{1cm} (2)

\(C_m\) is the highest initial Pb(II) and Ni(II) ions concentration (mg/L). The isotherm is described as: unfavorable when \(R_L > 1\), linear when \(R_L = 1\), favorable when \(0 < R_L < 1\) and irreversible when \(R_L = 0\). The \(R_L\) values obtained for the present study were all less than unity (Table 1) at the initial concentrations of 100 mg/L studied, showing that the isotherm was favourable under the conditions of this study and also indicated that the adsorbents could be good substrates for the removal of the metal ions from aqueous solutions.

Fig. 7: Langmuir isotherm plot of \(C_e/q_e\) vs \(C_e\) for adsorption of the metal ions onto chitosan
Fig. 8: Langmuir isotherm plot of Ce/qe vs Ce for adsorption of the metal ions onto activated charcoal

Fig. 9: Langmuir isotherm plot of Ce/qe vs Ce for adsorption of the metal ions onto composite adsorbent

Table 1: Langmuir Isotherm Constants for adsorption of Pb(II) and Ni(II) ions by the adsorbents

<table>
<thead>
<tr>
<th>Constants</th>
<th>Chitosan</th>
<th>Activated Charcoal</th>
<th>Composite adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_L (L/mg)</td>
<td>Pb(II)</td>
<td>Ni(II)</td>
<td>Pb(II)</td>
</tr>
<tr>
<td></td>
<td>0.1398</td>
<td>0.1067</td>
<td>0.1695</td>
</tr>
<tr>
<td>q_max (mg/g)</td>
<td>Pb(II)</td>
<td>Ni(II)</td>
<td>Pb(II)</td>
</tr>
<tr>
<td></td>
<td>55.25</td>
<td>49.26</td>
<td>70.42</td>
</tr>
<tr>
<td>R_L (C_0 = 100)</td>
<td>0.0668</td>
<td>0.0857</td>
<td>0.0557</td>
</tr>
<tr>
<td>R^2</td>
<td>0.9997</td>
<td>0.9995</td>
<td>0.9769</td>
</tr>
</tbody>
</table>

Equilibrium Freundlich Isotherm

The linearized form of Freundlich adsorption isotherm is represented as\textsuperscript{19}:

\[
\ln q_e = \ln k_F + \frac{1}{n} \ln C_e
\]  

(3)

Where K_F and n are Freundlich constants describing both capacity and the intensity of the adsorption process, respectively. Figures 10-12 are linear plots of ln q_e vs ln C_e, according to Freundlich isotherm equation. The constants K_F and n were calculated from the intercept and slope of the linear Freundlich plots and are presented in Table 2. Assessment of the R^2 values for the three adsorbents shows that the adsorption of the metal ions onto the granular activated charcoal was best described by the Freundlich model. The correlation coefficients (R^2) were generally high for the three adsorbents, indicating the fit of the experimental data into the isotherm. K_F is an approximate indicator of adsorption capacity while n indicates favourability and intensity of the
adsorbate/adsorbent systems. If \( n = 1 \) then the partition between the two phases are independent of the concentration. If the value of \( 1/n \) is below one, it indicates a normal adsorption but when greater than one indicates cooperative adsorption\(^{20}\), and \( n \) values between 1 and 10 represent favourable adsorption conditions\(^{21}\). In all cases reported here, the range of the values of \( n \) was within the range of 1.0311 to 1.0858 for the adsorption process indicating beneficial adsorption for the system under study. The high \( R^2 \) values suggest an excellent fitting of experimental data into the Freundlich model. The Freundlich constants and the \( R^2 \) values are presented in Table 2.

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**Fig. 10:** Freundlich isotherm plot of \( \ln q_e \) vs \( \ln C_e \) for adsorption of the metal ions onto chitosan

**Fig. 11:** Freundlich isotherm plot of \( \ln q_e \) vs \( \ln C_e \) for adsorption of the metal ions onto the activated charcoal

**Fig. 12:** Freundlich isotherm plot of \( \ln q_e \) vs \( \ln C_e \) for adsorption of the metal ions onto the composite adsorbent
Table 2: Freundlich Isotherm Constants for adsorption of Pb(II) and Ni(II) ions by the adsorbents

<table>
<thead>
<tr>
<th>Constants</th>
<th>Chitosan</th>
<th>Activated Charcoal</th>
<th>Composite adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_F</td>
<td>6.7160</td>
<td>4.6311</td>
<td>10.4594</td>
</tr>
<tr>
<td>N</td>
<td>1.0753</td>
<td>1.0858</td>
<td>1.0561</td>
</tr>
<tr>
<td>R²</td>
<td>0.9995</td>
<td>0.9994</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

Dubinin-Radushkevich Isotherm

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface\(^{21,22}\). The model has often successfully fitted high solute activities and the intermediate range of concentrations data well and is represented as:

\[
\ln q_e = \ln q_D - B_D \varepsilon^2 
\]

(4)

\[
\varepsilon = RT \ln \left( 1 + \frac{1}{c_e} \right) 
\]

(5)

where \( q_e \) = amount of Pb\(^{2+}\) and Ni\(^{2+}\) in the adsorbents at equilibrium (mg/g); \( q_D \) is the theoretical isotherm saturation capacity (mg/g) and \( B_D \) is the Dubinin-Radushkevich isotherm constant, which is related to adsorption energy (\( \text{mol}^2 \text{kJ}^{-2} \)). \( R \) is the gas constant (kJ mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the temperature (K). The isotherm is usually applied to distinguish the physical and chemical adsorption of metal ions onto the adsorbents with its mean free energy, \( E \) per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) being computed using the relation:

\[
E = \frac{1}{\sqrt{2B_D}} 
\]

(6)

One of the unique features of the Dubinin-Radushkevich (D-R) isotherm model lies in the fact that it is temperature-dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed (\( q_e \)) vs \( \varepsilon^2 \), the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve\(^{23}\). The linear plots obtained (Figs. 14 - 15) show the fit of the isotherm to the experimental adsorption data. The values of \( B_D \) and \( q_D \) were obtained from the slopes and intercepts of the linear plots and are presented in Table 3. Examination of the data shows that the Dubinin-Radushkevich isotherm provides the best description of the adsorption of the metal ions onto the composite adsorbent and this suggest that the characteristic sorption may be related to the porous structure of the adsorbent. The coefficients of correlation (\( R^2 \) values) were all high for the three adsorbents indicating that the model adequately described the experimental data.

Some researchers\(^{24-26}\) had reported that when the value of \( E \) is below 8 kJ mol\(^{-1}\), the adsorption process can be considered as physical adsorption and when it is within the range of 9–16 kJ mol\(^{-1}\), it is the chemical adsorption. From Table 3, it can be observed that the obtained values of mean free energy, \( E_D \) are limited within the range of 2.178 - 4.560 kJ mol\(^{-1}\), indicating that physisorption may have played a dominant role in the adsorption of Pb(II) and Ni(II) ions onto the adsorbents.

![Fig. 13: Dubinin-Radushkevich isotherm plot of ln qe vs $\varepsilon^2$ for adsorption of the metal ions onto chitosan](image-url)

Fig. 13: Dubinin-Radushkevich isotherm plot of ln qe vs $\varepsilon^2$ for adsorption of the metal ions onto chitosan

\[
y = -0.7735x + 2.1361 \quad R^2 = 0.9369 
\]

\[
y = -1.0545x + 2.0578 \quad R^2 = 0.9209 
\]
CONCLUSION
This study investigates the potential of three adsorbents- chitosan, activated charcoal and a combination of both (composite adsorbent) in removing two heavy metal ions: Ni$^{2+}$ and Pb$^{2+}$ from aqueous solutions. The influences of pH and concentration on the process were examined. The equilibrium experimental data were tested with three isotherm models- the Langmuir, Freundlich and Dubinin-Radushkevich isotherms. Assessment of correlation coefficients for the three models shows that Langmuir provided the best description for adsorption of the metal ions onto chitosan, Freundlich gave best interpretation for adsorption of the metal ions onto activated charcoal while adsorption onto the composite adsorbent was best described by the Dubinin-Radushkevich isotherm. Assessment of the maximum amount of metal ion adsorbed onto
the three adsorbents showed that Pb\textsuperscript{2+} ions were better adsorbed than Ni\textsuperscript{2+}. The affinity of adsorbents for the metal ions also follows the trend: composite adsorbent > charcoal > chitosan, indicating that the composite adsorbent may have provided a great synergistic effect that lead to enhanced removal of the metal ions by the adsorbent. Results obtained from pH variation show that the optimum pH for adsorption of Pb\textsuperscript{2+} and Ni\textsuperscript{2+} onto chitosan and activated charcoal occurred at 6.0 while that of the composite adsorbent displayed a different pH dependence with Pb\textsuperscript{2+} having maximum adsorption at a pH 4.0 and Ni\textsuperscript{2+} at pH 6.

REFERENCES


