INTRODUCTION

Inorganic heavy metal species and related metalloids are among the most problematic contaminants in surface water due to their challenging removal processes, complicated existence, minuscule concentration in large volumes, and competition with nontoxic inorganic species (Al-Bayati et al., 2023; Mohammmed et al., 2023; Waisi et al., 2015). Pb(II) is recognized as a longstanding environmental contaminant. It exists in various industries, including acid battery manufacturing, ceramic and glass factories, printing, tanning, photographic materials, metal planting and finishing (Momčilović et al., 2011). Pb(II) is a common metal with a harmful impact on the environment and the danger of water pollution for humans. Extended periods of Pb(II) exposure may result in infertility and miscarriage, in addition to causing damage to the health and nervous system of human (Dave and Chopda, 2014). Such a toxic material was needed to be extracted from the drainage system. A trace concentration of Pb(II) ions is also extremely hazardous (Wani et al., 2015). The permissible Pb(II) concentration in potable water, as mandated by the Environmental Protection Agency (EPA) of the United States, is 0.015 mg/L. The most common treatment technologies for metal ions elimination are precipitation (Onundi et al., 2011), phytoremediation (Saxena et al., 2020), electrocoagulation (Shakir and Husein, 2009), and ion exchange (Chanthapon et al., 2018). Membrane technology is considered an efficient method to treat polluted water, but its disadvantages are high energy consumption and fouling. In addition, the adsorption treatment method is widely used for heavy metal removal because of its consistency and simplicity (Kalash et al., 2020). To adsorb a trace amount of pollutants, especially heavy metals, the adsorbent material, such as activated carbon, should

Adsorption Isotherms and Kinetics Studies of Lead on Polyacrylonitrile-Based Activated Carbon Nonwoven Nanofibres

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ABSTRACT

Activated carbon nonwoven nanofibres (ACNN) mat derived from polyacrylonitrile was manufactured through the electrospinning method followed by thermal treatment steps. The ACNN ability to adsorb Pb(II) from a liquid solution was evaluated. The fabricated ACNN was characterized using scanning electron microscope, Fourier-transform infrared spectroscopy, and Brunauer-Emmett-Teller method. The resulting ACNN exhibited nanofibres with a diameter of 530 nm and a surface area of 550 m²/g. Various adsorption experiments were performed in batch scale to study the impact of factors like contact time, initial Pb(II) ions concentration, and pH. At pH 5, ACNN achieved a removal efficiency of 98% of Pb(II). The equilibrium data for Pb(II) ions was analysed using the Freundlich and Langmuir isotherm models. Both kinetic models (pseudo-first-order and pseudo-second-order) and isotherm models were tested. Results revealed that the Langmuir model accurately described the adsorption isotherm of Pb(II) with a maximum capacity of 15.72 mg/g. Data analysis suggested that the pseudo-second-order model better represented the kinetic adsorption behaviour of Pb(II).

Keywords: activated carbon, adsorption, Pb(II), nanofibres.
have a large surface area, unique microstructure, high adsorption capacity, and good selectivity. Nano-form adsorbent materials such as nanoparticles, nanotubes, and nanofibres are widely applied in extracting the dissolved heavy metal ions (Dave and Chopda, 2014). Activated carbon nonwoven nanofibres (ACNN) are nanofibre form adsorbents. They are fabricated by electrospinning method followed by thermal treating steps. In the electrospinning technique, the precursor nanofibres are created from polymeric solution in a voltage field to overcome the surface tension of the polymeric droplet. Commonly, the polyacrylonitrile (PAN) polymer is used in preparing ACNN, because of its yield and thermal characteristics (Waisi, 2019). The thermal treatment stage consists of carbonisation under the N$_2$ atmosphere at a temperature of 800 °C to convert the precursor fibres to carbon fibres. Then, the activation stage can be physically (using steam) or chemically (using chemicals such as H$_2$SO$_4$ and HNO$_3$) processed at high temperatures (Fan et al., 2011). The ACNN generated displays features like having a surface area that is easy to access pores of moderate size and fibres on a nanoscale (Waisi et al., 2023). This specific carbon material has been utilised in energy storage, cleaning air and treating water (Alkarbouly and Waisi, 2022; Waisi et al., 2020). The ACNN mats have been applied to remove contaminants like cations, toluene, formaldehyde and emulsified oil (Oh et al., 2008; Waisi et al., 2020, 2023). However, little attention has been focused on using the ACNN material for adsorption of heavy metals. The adsorption capacity of heavy metals is mainly affected by the porous structure and the surface chemistry of the adsorbent material. Using the electrospinning technique can help in producing aligned nanofibres. Then, controlling the carbonization and Activation stages can provide the nanofibre material with the necessary functional groups that increase the interaction between heavy metal ions and ACNN fibres. In this work, the electrospinning method fabricated the PAN-based ACNN sheet. Then, the surface morphology, pores construction, and surface chemistry of the fabricated ACNN sheets were explored by SEM, BET, and FTIR analysis. Then, it was applied in Pb(II) removal from water using batch mode tests to understand the isotherm and kinetics of the process by investigating the effect of the initial solution pH and ACNN sheets dose over time.

**MATERIALS**

Polyacrylonitrile (Mwt. = 150,000 g/mol) was ordered from Scientific Polymer Products Inc. N,N-dimethylformamide (DMF) was obtained from Sigma Aldrich (USA). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were acquired from Sigma Aldrich, United States of America. Analytical grade of Pb(NO$_3$)$_2$ (purity = 99% and Mwt. = 331.2 g/mol from Sigma Aldrich, USA) was used to prepare 1000 mg/L standard stock solution of Lead (II).

**Preparation of the adsorbent**

A certain amount of the polymer is mixed with the DMF solvent under a continuous mixing for 2 h at 60 °C to prepare 12 wt.% PAN/DMF. The precursor solution was dispensed using an electrospinning system fitted with a revolving 70 rpm grounded collector tank. A high pressure syringe pump (KD Scientific) fitted as an electrospinning nozzle with a needle of 20 gauges to deliver the polymer solution to the collector drum. The voltage applied was 21 kV with a fixed distance from the collector (18 cm). The fabricated precursor nanofibre mats were then stabilised in the air in a muffle furnace (Carbolite) at 280 °C for 1 h with 1°C/min ramp rate. After carbonisation and activation, the stabilised nanofibres were transformed into activated carbon nonwoven nanofibres. The carbonisation step was carried out in a furnace (Thermo Scientific Lindberg Blue M Tube Furnace) in an N$_2$ gas at 650 °C within 1 h with a 3 °C/min ramp rate. Then, the activation process was carried out in the same furnace with steam (60 g/h) at 750 °C for 1 h to produce the activated carbon nonwoven nanofibres. Authors’ previous research describes the optimal conditions in detail (Waisi et al., 2019).

**The characterizations**

The scanning electron microscopy technique was used to examine the surface structure of ACNN using (FESEM, JEOL 6335F). The functional groups accountable for the binding of lead ions were identified using an Fourier-transform infrared spectroscopy (FTIR) within the 4000–500 cm$^{-1}$ region. Micromeritics instrument
corporation analyzer was used for determining N₂ adsorption/desorption isotherms on the adsorbent material. The precise surface area of every sample was determined by utilising the Brunauer-Emmett-Teller (BET) model. The supernatant liquid was analysed at different time intervals using ICP-MS after separating the ACNN with nitrocellulose filter paper to make it adsorbent-free. The dissolved Pb(II) samples were acidified to 2% HNO₃ (trace metal grade) and examined using a plasma-mass spectrometer that is inductively linked (Agilent 7700x with Helium collision cell, ICP-MS).

**Batch adsorption experiments**

The simulated lead ions solution was prepared by diluting the prepared standard stock solution of Pb(II) with distilled water. Batch experiments were carried out by contacting 200 mg ACNN with 250 ml of Pb(II) solution in a plastic flask to determine the adsorption isotherms of Pb(II) on ACNN. The experiments were performed using a magnetic stirrer (400 rpm) at room temperature for 5 h. The impact of adsorption factors on the rate of the removal process were observed by varying ACNN dose (25, 50, and 200 mg) and initial solution pH (3, 4, 5, and 6) over time. The retained Pb ions concentration in the adsorbent phase (q) and the removal percentage (R%) were calculated according to Equations 1 and 2, respectively.

\[
q = (C_i - C_t) V/W \quad (1)
\]
\[
R (%) = (C_i - C_t) \times 100/C_i \quad (2)
\]

The \(C_i\) is the initial Pb(II) concentration (mg/L); \(C_t\) is the Pb(II) concentration in the solution during the experiment (mg/L); \(V\) is the aqueous solution volume (L); and \(W\) is the weight (g) of ACNN. All experiments were duplicated, and the average result was depended for the further calculation. The flasks were sealed and stopped off to prevent pH fluctuations caused by gas exchange throughout the experiment.

**RESULTS AND DISCUSSION**

**The characterization of ACNN**

Figure 1 displays the surface morphology and cross-sectional scanning electron micrographs of ACNN sheets based on 12% PAN/DMF. Figure 1a shows the surface morphology of the ACNN sheet, which consists of long, continuous, and beads-free nanofibers in a nonwoven structure. The average fibre size was about 530 nm, with a homogeneous size distribution. According to the ACNN sheets, cross-sectional morphology

![Figure 1](image1.png)

**Figure 1.** The images in SEM of the prepared ACNN sheets: (a) surface and (b) cross-section morphologies

![Figure 2](image2.png)

**Figure 2.** The ACNN analysis (a) FTIR spectrum and (b) pore size measurement from BET analysis
(Figure 1b) has a nonwoven structure with a thickness of approximately 160 µm.

The FTIR surface chemistry of ACNN sheets is illustrated in Figure 2a. The primary peak group seen at 1160 cm\(^{-1}\) is associated with the phenolic group’s O-H bond produced by the steam activation step. The intensity of the peak at 1580 cm\(^{-1}\) increases along with carbonyl groups during the activation by steam (Karra et al., 2013). Denitrogenation reactions occur in the activation stage, facilitating the elimination of structural imperfections and non-carbon components (including sulphur, oxygen, and nitrogen) while also contributing to forming sheet-like structures.

Furthermore, typical N\(_2\) adsorption/desorption isotherm for ACNN is illustrated in Figure 2b. Under the IUPAC classification, this is called type II adsorption. According to the adsorption isotherm of ACNN, most pores were microporous and mesoporous, measuring less than 50 nm in diameter.

**Impact of the adsorption parameters**

**Impact of pH solution**

While holding all other parameters constant (5% initial ion concentration and 0.2 g ACNN dosage, Figure 3 illustrates the Pb(II) removal by ACNN mats at various pH levels. At a pH of 5, the maximum degree of Pb(II) elimination was 98%. A clear improvement in the efficacy of Pb(II) adsorption was noted when the pH of the aqueous solution rose from 3 to the optimal value of 5. The fabricated ACNN absorb Pb(II) under acidic conditions with reduced efficiency, as seen by the subsequent dramatic decrease in value with decreasing pH. This may be deduced from the pH\(_{\text{PZC}}\) value, representing the zero charge point for activated carbon nanofibers. The pH\(_{\text{PZC}}\) ranges from 5 to 6 (Mahmood and Waisi, 2021). At pH values below pH\(_{\text{PZC}}\), the surface of ACNN mats exhibits a positive charge, whereas it demonstrates a negative charge above that point. When the surface is positively charged, adsorption sites become encased in hydronium ions (H\(_3\)O\(^+\)). As a result, the repulsive interactions between metal ions and adsorbent surfaces diminish. Hence, an adsorption process is more effectively conducted at a pH greater than pH\(_{\text{PZC}}\). Nevertheless, as the pH level approaches or exceeds six, the metal ions precipitate as salts, impeding the adsorption.

**Impact of adsorbent dosage**

According to Figure 4, the adsorption of Pb (II) ions increased as the adsorbent amount was raised from 25 mg to 200 mg because of increasing the availability of adsorbing sites at elevated doses. The maximum adsorption was recorded at the ACNN dose of 200 mg with 98% elimination of Pb(II) ions.

**Impact of contact time**

The influence of contact time on the uptake of Pb(II) ions on ACNN is illustrated in Figure 5. The obtained result showed a rapid increase in the Pb(II) ions uptake on ACNN material in the first 1 hr to reach 92% removal percentage due to the fast interactions between the effective sites of the (ACNN) adsorbent and the accumulation of

![Figure 3](image1.png)  
**Figure 3.** Impact of the solution pH on Pb(II) ions adsorption on ACNN. The experiment conditions were 25 °C, 400 rpm, 200 mg ACNN, and 5 mg/L initial Pb(II) concentration

![Figure 4](image2.png)  
**Figure 4.** The impact of ACNN dose on the effectiveness of adsorption. The experiment conditions were 25 °C, 400 rpm, pH = 5, and 5 mg/L initial Pb(II) ions concentration
Pb(II) ions on the adsorbent surface. This can be explained by the fact that the high porous structure of ACNN offers a lot of binding sites on the adsorbent surface. The less plentiful supply of active causes the Pb(II) ions adsorption to become constant once it reaches equilibrium.

**Adsorption isotherm**

Langmuir and Freundlich isotherm models are represented by:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{1}{q_{\text{max}}} \times C_e \tag{3}
\]

\[
\log q_e = \log K_F + \left(\frac{1}{n}\right) \times \log C_e \tag{4}
\]

where: the equilibrium Pb(II) ions concentration is \(C_e\) (mg/L), the Pb(II) amount adsorbed at equilibrium is \(q_e\), the maximum adsorption capacity is \(q_{\text{max}}\), the power of the isotherm is \(n\), and the equilibrium constants of Langmuir and Freundlich models are \(K_L\) and \(K_F\), respectively. Figure 6 shows that Pb ions adsorption data fitted Langmuir model more than Freundlich model.

**Kinetic modelling**

The pseud-first and pseudo-second order kinetic models were applied to examine Pb(II) adsorption kinetic characteristics onto ACNN. These models can be represented in linear form as follows:

\[
\log (q_e - q) = \log q_e - \left(\frac{k_1}{2.303}\right) \times t \tag{5}
\]

\[
t\frac{1}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_i} \times t \tag{6}
\]

where: \(q_e\) and \(q_i\), in mg/g, represent the Pb(II) adsorption uptake at equilibrium and at time \(t\), respectively, and \(K_1\) and \(K_2\) is the constant of adsorption rate in the first and second order kinetic models, respectively. The adsorption rate constants \(K_1\) and \(K_2\) and the quantity of adsorption in equilibrium \(q_e\) are predicted using the slope and intercept of the linear plot (Figure 7), with the findings presented in Table 2.

**Table 1.** The coefficients of Langmuir and Freundlich models for the adsorption of Pb(II) on ACNN

<table>
<thead>
<tr>
<th>Adsorption isotherm model</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>(q_{\text{max}}) (mg/g)</td>
<td>15.72</td>
</tr>
<tr>
<td></td>
<td>(K_L)</td>
<td>8.26</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.992</td>
</tr>
<tr>
<td>Freundlich</td>
<td>(K_F) (mg/g)</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>(n)</td>
<td>3.19</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.762</td>
</tr>
</tbody>
</table>

**Figure 5.** The effectiveness of ACNN in Pb(II) adsorption over time. The experiment conditions were 25 °C, 400 rpm, 200 mg ACNN, pH = 5 and 5 mg/L initial Pb(II) ions concentration

**Figure 6.** The Pb(II) adsorption isotherm models on ACNN (a) Langmuir (b) Freundlich. The experiment conditions were 25 °C, 400 rpm, 200 mg ACNN, 5 mg/L initial Pb(II) ions concentration, and 5 h contact time.
Table 2. Rate constants for lead adsorption on ACNN

<table>
<thead>
<tr>
<th>Adsorption kinetic model</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>$q_e$, mg/g</td>
<td>1.5077</td>
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<tr>
<td></td>
<td>$K_1$, 1/min</td>
<td>1.76</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.764</td>
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<tr>
<td>Pseudo-second-order</td>
<td>$q_e$, mg/g</td>
<td>6.04</td>
</tr>
<tr>
<td></td>
<td>$K_2$, g/mg. min</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

**Figure 7.** Adsorption kinetic models for Pb adsorption on ACNN (a) pseudo-first and (b) pseudo-second order

**CONCLUSIONS**

This work included preparing the activated carbon nonwoven nanofibres via the electro-spinning method using polymeric precursor solution (PAN/DMF) and thermal treatment. The prepared ACNN was applied to remove Pb(II) ions from water. This research aimed to examine the effects of pH, adsorbent dose, and contact duration using batch sorption. Because no more sites were available for the adsorbent to capture Pb(II) ions, the adsorption was at its quickest after 30 minutes and remained almost constant after one hour. Lead removal efficiency of 98% was achieved at pH 5 with respect to lead ion removal. Furthermore, the results show that the prepared ACNN had excellent adsorption efficiency of Pb(II) due to its unique characteristics, such as the porous structure, the accessible high surface area, and the effective chemical functional groups on the surface.

**REFERENCES**


