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SUSTAINABLE ABATEMENT OF LEAD (II) FROM WATER VIA HYDROCHLORIC ACID TREATED-ACTIVATED CHARCOAL DERIVED FROM PEANUT SHELLS: EQUILIBRIUM, ISOTHERM AND KINETICS MODELING

M. A. K. Azad[1,✉], M. A. Anwar[2], and R. Ranjan[3]
[1]Department of Applied Sciences and Humanities (Chemistry), Darbhanga College of Engineering, Darbhanga-846005, (Bihar) India.
[2]Department of Mechanical Engineering, Darbhanga College of Engineering, Darbhanga-846005, (Bihar) India.
[3]Department of Chemistry, Marwari College, L.N.M.U, Darbhanga-846004, (Bihar) India.
✉Corresponding author: aazadchem30@gmail.com

ABSTRACT
The current research was conducted to study the efficiency of hydrochloric acid-chemically treated activated charcoal of peanut shells as a biosorbent for Pb (II) ions adsorption in water. The adsorption process was optimised by evaluating the impact of key variables like pH, contact time, biosorbent dosage and initial lead ions concentration. The optimum conditions for Pb (II) ions adsorption were observed at pH 6, an agitation time of 120 minutes, biosorbent dosage of 1.5 g and an initial Pb (II) ions concentration of 60 mg/L. Under these conditions, Hydrochloric acid-treated activated charcoal derived from peanut shells showed significant adsorption efficiency of 90.2% lead (II) contaminants in water and exhibited a maximum adsorption capacity of 43.85 mg/g, highlighting its potential as an economically viable and eco-friendly sustainable adsorbent for Pb^{2+} ions removal from contaminated water. The experimental adsorption data exhibited a strong correlation with the Langmuir isotherm model, having an R^2 value of 0.9925, suggesting a strong correlation with chemical interaction mechanisms. Kinetics evaluation revealed that Pb (II) ions adsorption followed the pseudo-second order model accurately, demonstrating a better correlation, as supported by the high correlation coefficient (R^2) value of 0.9845. The results suggest that chemically modified peanut shells activated charcoal has promising potential for the abatement of lead (II) ions from polluted water. This investigation provides valuable insights into the application of plant and agricultural waste-based adsorbents for sustainable environmental remediation and pollution control.
Key-words: Biosorption, Peanut Shells Activated Charcoal, Pb (II) Adsorption, Isotherm, Kinetics.
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INTRODUCTION

Heavy metals in water bodies pose a significant environmental and human health concern as well as a serious threat to aquatic animals because of their harmful effects, long-lasting presence and ability to bioaccumulate in the food chain. Abatement of heavy metals from polluted water bodies has remained a primary concern because these are not only causing contamination of water bodies but are also toxic to many forms of life. Thus, its removal from water continues to pose a significant challenge for researchers.[1,2] Since most of the heavy metals cannot be transformed into non-toxic forms, it is imperative to reduce their concentrations within permissible limits before environmental discharge. Failure to do so could pose significant risks to human health and aquatic ecosystems. Due to the toxic nature of heavy metals like arsenic, chromium, mercury and lead, they are considered the most immediate concerns for their removal. The present work evaluated the abatement of lead (II) ions from water systems as a bioremediation technique. Many research studies have been conducted in this area.[3,4] However, the focus of the current research is on developing an economically viable, cost-effective, sustainable and readily available method that is simple and easily accessible to the common people. Water contamination by lead is a significant global concern due to its severe health risks and environmental impacts. Lead (Pb) is a toxic heavy metal that contaminates water bodies through various natural sources like weathering of rocks and soils, and volcanic activity as well as anthropogenic sources such as industrial discharge, mining,

battery manufacturing, metal plating, paints, pigments, vehicle emission, road runoff, corroded plumbing systems, lead solder, Landfill leachate, pesticides, etc. Consumption of lead causes neurological damage, developmental delays and learning disabilities in children. In adults, prolonged exposure to lead can result in cardiovascular problems, kidney damage and other chronic illnesses. Lead can accumulate in aquatic organisms and disrupts ecosystems by entering the food chain. WHO has regulated drinking water concentration not to exceed 0.01 mg/L for lead. The persistence and bioaccumulation tendency of lead in the food chain make its removal from water a critical priority and this drew attention to the development of an effective method for its removal. Traditional water treatment methods are often insufficient to address lead contamination and several techniques have been employed, including chemical precipitation, adsorption, ion exchange, membrane filtration, membrane separation, resin ion exchange and electrochemical methods, each with its own advantages and limitations besides being expensive. Hence, a revised approach that is both optimal and affordable must be developed. Recently, Contemporary research works have focused on the remediation of hazardous metals from aqueous effluents through biosorption using plant and agricultural by-products.[5,6] Biosorption has emerged as a significant method for controlling water pollution by removing heavy metals from aqueous systems. The newly developed biosorbents are characterised by their high versatility, selectivity for metals and exceptional uptake capacity. The present work aims to evaluate the effectiveness of activated charcoal derived from easily available peanut shells as a biosorbent for the abatement of hazardous metal pollutants like Pb (II) ions. The batch adsorption studies have been conducted in relation to parameters like pH, contact time, adsorbent dosage and initial concentration of metal ions and correlated to isotherms and kinetics data.

EXPERIMENTAL

Preparation of Activated Charcoal Powder from Peanut Shells

Discarded Peanut shells were cleaned using distilled water to eliminate contaminants and particulate matter. The cleaned peanut shells were oven-dried at 90 ^{0}C for 24 hours to ensure removal of moisture, followed by grinding into fine particles. A steel cylindrical vessel filled with dried peanut shells powder was sealed to maintain an oxygen-free environment throughout charring and heated in the furnace at a temperature of 400°C for 2 hours, which converted the organic material into carbonised char. The carbonised char was then activated by mixing with an activating agent- hydrochloric acid and kept the mixture for 24 hours at room temperature for uniform soaking in 1 M HCl. After soaking, the activated charcoal was rinsed with distilled water to wash away excess chemical activating agent (HCl) till the pH of the washed water is neutral.[7] Thereafter, the washed activated charcoal was dried in an oven at 60°C for 24 hours and the resultant fine black adsorbent was sieved through a standard 100 μm mesh to produce uniformly sized activated charcoal particles for further use. A further fine adsorbent particle size (< 100 μm) was not considered owing to significant difficulty in the separation of the fine activated charcoal particles from the solution.

Preparation of Stock Solution

A 1000 mg/L Pb (II) stock standard preparation was made by dissolving 1.598 g of $Pb(NO_3)_2$ in 1 L of demineralised water. Subsequently, dilution of the stock solution was performed serially to achieve the required concentrations for further experiments.

Batch Adsorption Studies

To evaluate the adsorption performance of the adsorbent toward Pb (II) ions in aqueous solution, a batch study was carried out by varying experimental parameters as a function of pH of solution, contact time, adsorbent dosage and initial concentration of metal ions in the solution.[8,9] Role of solution pH on the adsorption efficiency of Pb (II) ions was evaluated within a pH range of 3 to 9 using 0.1 M HCl or NaOH. For this, 1 L $Pb(NO_3)_2$ solution prepared at an initial concentration of 60 mg/L was taken and pH was systematically adjusted across the acidic to alkaline range by maintaining a contact time of 120 minutes and a fixed adsorbent dose of 1.5 g uniformly. The effect of contact time was studied by taking a 1 L aqueous solution of 60 mg/L Pb^{2+} ions concentration, keeping a fixed adsorbent mass of 1.5 g at pH 6.0, with varying time periods of 20 minutes, 40 minutes, 60 minutes, 80 minutes, 100 minutes, 120 minutes, 140 minutes and 160 minutes. The effect of adsorbent dosage was performed by taking 1 L aqueous

solution having a concentration of Pb^{2+} ions at 60 mg/L with varying masses of activated charcoal powder of peanut shells as 0.25 g, 0.5 g, 0.75 g, 1 g, 1.25 g, 1.5 g, 1.75 g, 2 g, 2.25 g and 2.5 g at pH 6 for 120 minutes. To evaluate the initial concentration effects, 1 L of Pb (II) solution prepared at varying concentrations from 10 to 80 mg/L was placed together at pH 6 using a constant mass of activated charcoal powder of peanut shells (i.e., 1.5 g) for 120 minutes of agitation time. All experiments were performed at room temperature. Following each experimental run, the solution was immediately filtered and subsequently, residual contents of lead (II) ions in the filtrate was analysed by the Dithizone procedure using a UV-visible spectrophotometer.[10]

The following equation was applied to compute the percentage removal efficiency of Pb (II) ions:

$$\% \text{ Removal of lead} = \frac{(Ci - Ce)}{Ci} \times 100 \qquad (1)$$

Where C_i and C_e represent initial lead (II) ions concentration (mg/L) before adsorption and final (i.e. equilibrium) lead (II) ions concentration (mg/L) after adsorption, respectively.

RESULTS AND DISCUSSION

Biosorption Studies

Effect of pH of solution

pH is a significant parameter for adsorption efficiency because variation in pH decides the charge density on the surface of adsorbents, oxidation state of adsorbates and the overall adsorption capacity. The experiments were performed over pH conditions from 3 to 9 using 0.1 M HCl or NaOH. Thus, the removal efficiency of lead (II) ions reached a maximum of 90.2% at pH 6 and showed a gradual decline beyond this optimum pH due to the onset of precipitation as hydroxide (Fig.-1). Similar results have been reported by researchers.[11-13] The Preliminary analysis suggested that the driving forces accountable for the uptake of lead (II) ions by the adsorbent might be electrostatic forces, complexation and chelation at the active sites of the adsorbent. The adsorption efficiency showed a decreasing trend below pH 6, which was supposed to abundance of H^+ ions, which compete with lead (II) ions for adsorption sites occupancy on the surface-active regions of the adsorbent. Thus, the adsorption efficiency achieved its highest at optimum pH 6, as H^+ ions became insignificant and increased lead (II) ions uptake was observed on the adsorbent's surface.

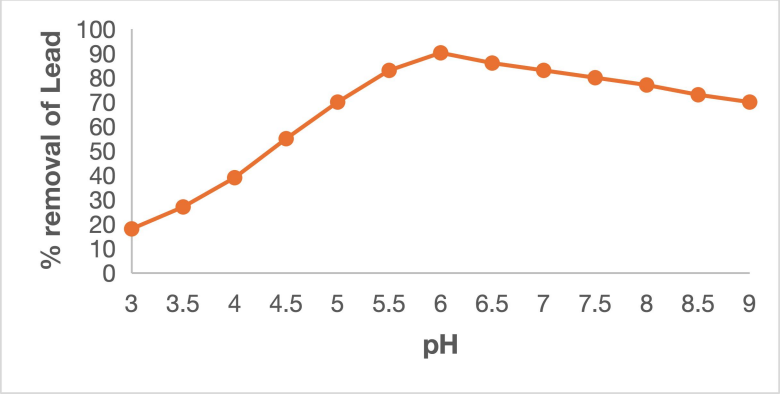

Fig.-1: pH-Dependent Adsorption of Pb (II) Ions on Activated Charcoal Derived From Peanut Shells.

Effect of Contact Time

The solid-liquid interaction duration is a significant factor affecting the adsorption efficiency and adsorption equilibrium.[14-16] To evaluate the impact of the interaction period for lead (II) ions removal efficiency, experiments were conducted with agitation time ranging from 20 to 160 minutes at pH 6 with a fixed mass (1.5 g) of adsorbent. Initially, a rapid adsorption was observed because of the abundance and availability of active centres on the adsorbent surface. The adsorption efficiency achieved a maximum of 90.2 % of lead (II) ions at 120 minutes of agitation time, called as equilibrium time and subsequently, the adsorption rate declined and no substantial uptake of Pb (II) ions was observed. Therefore, 120 minutes was established as the equilibrium contact time for further investigations. The results are shown in Fig.-2.

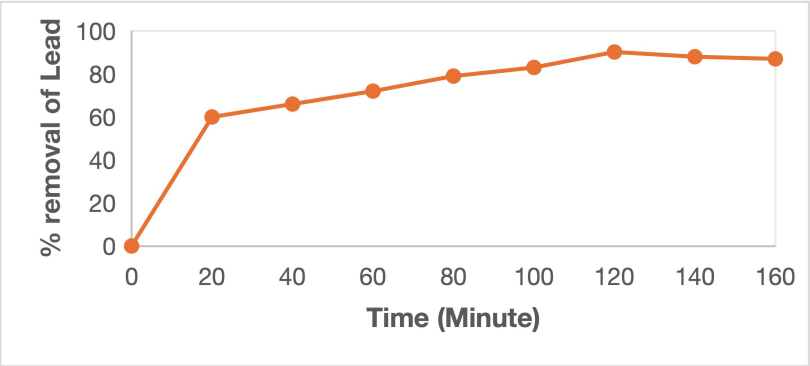

Fig.-2: Time-Dependent Adsorption of Pb (II) Ions on Activated Charcoal Derived From Peanut Shells

Effect of Adsorbent Dosage

Adsorption efficiency and capacity are directly governed by adsorbent dosage. The surface binding sites of the adsorbent control the effectiveness of adsorption, which is largely dependent on its structural and chemical characteristics. The effect of dosage of peanut shells activated charcoal powder on the adsorption efficiency of lead (II) ions was analysed by employing adsorbent dosages varying from 0.25 to 2.5 g per litre of solution at pH 6 for 120 minutes with an initial concentration of 60 mg/L, as revealed in Fig.-3. The findings revealed that an upward trend in lead ions removal efficiency up to 1.5 g of biosorbent dosage and achieved equilibrium at 90.2% Pb (II) ions removal and beyond this, further increase did not remarkably improve removal efficiency.[17,18] Consequently, at equilibrium, the adsorption efficiency of Pb^{2+} ions decreased as the biosorbent dosage exceeded 1.5 g, which was attributed to reduced concentration gradient. Once the dispersion of lead (II) ions between the solid and liquid phases attained equilibrium, no significant adsorption was observed beyond 1.5 g of adsorbent dosage. Accordingly, 1.5 g/L was fixed as the standardised adsorbent dosage for subsequent investigations.

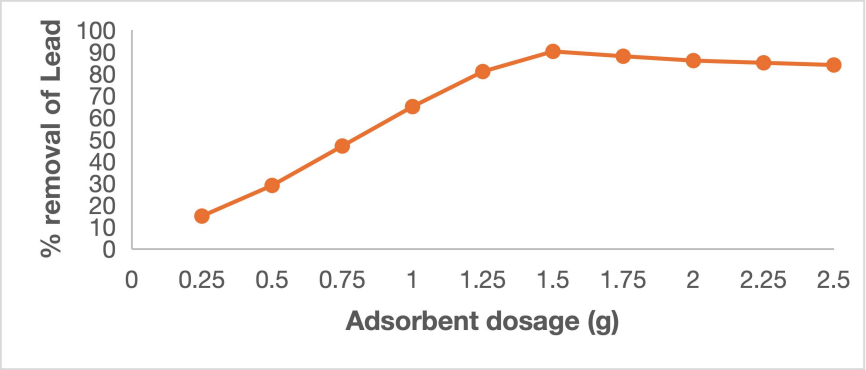

Fig.-3: Adsorbent Dosage-Dependent Adsorption of Pb (II) Ions on Activated Charcoal Derived From Peanut Shells

Effect of Initial Metal Ions Concentration

The adsorption efficiency was significantly influenced by the initial concentration of lead ions in the solution. The response to a change in initial lead (II) ions concentration was systematically assessed over the range of 10–80 mg/L. The experiment revealed that the adsorption efficiency for lead (II) ions by activated charcoal of peanut shells optimised at a concentration of up to 60 mg/L, and beyond this, no further adsorption occurred, indicating saturation of the active sites of the adsorbent's surface. Maximum lead (II) ions sequestration was achieved at 90.2%. A further increase in the initial concentration resulted in saturation of active sites, lowering their availability for accommodating excess Pb^{2+} ions in aqueous solution. Accordingly, an initial concentration of 60 mg/L was maintained throughout for the whole subsequent analysis.

Adsorption Isotherm Modeling

The uptake of Pb (II) ions by activated charcoal obtained from peanut shells was facilitated through surface coordination, ions substitution and coulombic interaction mechanisms.[19,20] The occurrence of

functional groups on activated charcoal derived from peanut shells was supposed to contribute to a potential influence on the adsorption mechanism.
The adsorption capacity (q_e) was determined using the following equation:

$$\text{Adsorption capacity } (q_e) = \frac{(Ci - Ce) \times V}{W} \quad (2)$$

Where C_i, C_e, W and V represent initial concentration of Pb^{2+} ions (in mg/L), equilibrium concentration of Pb^{2+} ions (in mg/L), mass of adsorbent (in g) and volume of solution (in L), respectively.
Equilibrium adsorption characteristics were quantitatively examined by fitting the data to both the Langmuir and the Freundlich isotherm equations.

Langmuir Adsorption Isotherm
The Langmuir model describes adsorption as a monolayer formation occurring uniformly over a surface containing a limited set of binding sites. The Langmuir adsorption isotherm is mathematically described by the following fundamental expression:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Here, Ce denotes the equilibrium concentration of Pb (II) ions (mg/L), q_e is the absorbed amount of Pb (II) per gram of adsorbent at equilibrium (mg/g), q_m signifies the theoretical maximum adsorption capacity (mg/g) and K_L refers to the Langmuir constant reflecting the strength of the adsorbate–adsorbent interaction (L/mg).
Upon linearization, the equation takes the form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

Freundlich Adsorption Isotherm
The Freundlich isotherm characterises adsorption occurring in multiple layers over surfaces with non-uniform energy distributions and is formulated as:

$$q_e = K_F C e^{1/n} \quad (5)$$

Where K_F refers to the extent to which an adsorbent can accommodate adsorbate molecules and n characterises the adsorption intensity of the adsorbent's surface.
The linearised relationship is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Table-1: Isotherm Parameters for Pb (II) Ions Uptake from Aqueous Solution on Activated Charcoal Powder

Parameters	Langmuir isotherm	Freundlich isotherm
Isotherm Constant	K_L = 0.704 L. mg^{-1}	K_F = 15.97
q_m (mg. g^{-1})	43.85	-
n	-	1.947
R^2	0.9925	0.9846
Adsorbent	Activated charcoal of Peanut shells	Activated charcoal of Peanut shells

Adsorption Kinetics Studies
To investigate adsorption kinetics, a series of experiments was systematically performed using 1 L aqueous solutions with a fixed dosage (1.5 g) of adsorbent and a fixed initial concentration (Ci = 60 mg/L) of Pb (II) ions. To ensure uniform mixing, the solutions were kept in constant agitation using a magnetic stirrer for progressively longer time intervals. After completion of each run, the solution was filtered and the filtrate was analysed to determine residual Pb (II) ion contents. The experimental results were evaluated by applying various kinetics models to determine the best-fitting adsorption behaviour.[21-23]

Pseudo-First-Order Kinetics
The Lagergren equation for pseudo-first-order kinetics is represented as follows:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (7)$$

Where, q_e = Amount of Pb^{2+} ions adsorbed at equilibrium (mg/g), q_t = Amount of Pb^{2+} adsorbed at time t (mg/g), K_1 = Pseudo-first order rate constant (min^{-1}) and t = Contact time (minutes).

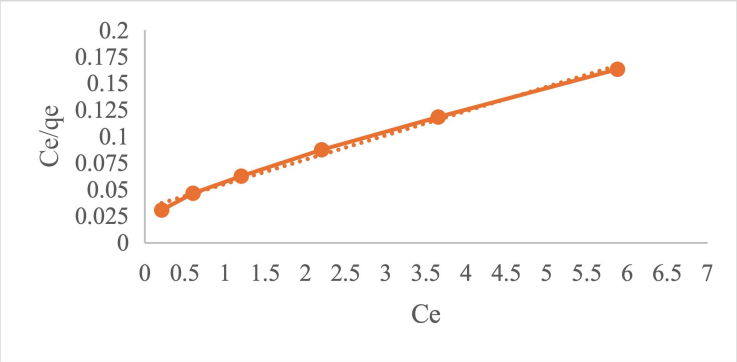

Fig.-4: Langmuir Isotherm of Pb (II) Ions Adsorption on Activated Charcoal Powder Derived From Peanut Shells

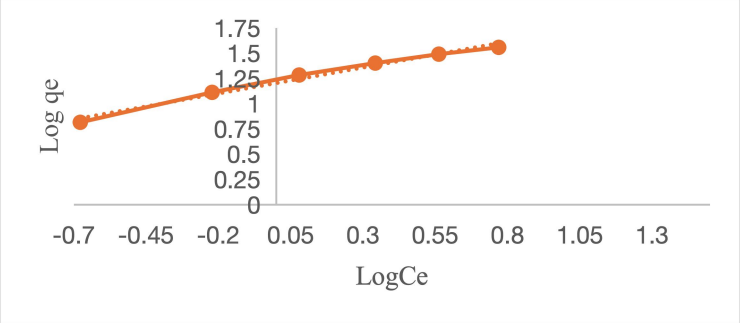

Fig.-5: Freundlich Isotherm of Pb (II) Ions Adsorption on Activated Charcoal Powder Derived From Peanut Shells

The integrated linearised equation is represented by the following expression:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (8)$$

Pseudo-Second Order Kinetics

This kinetics model proposes that the adsorption rate is governed by the squared abundance of free active sites remaining on the adsorbent surface. The rate expression for pseudo-second order chemisorption kinetics is described by the following equation:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (9)$$

The integrated linear equation is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Where, K_2 represents Pseudo-second order rate constant (g. mg^{-1}. min^{-1}).

Table-2: Kinetics Variables for the Uptake of Pb (II) Ions in the Aqueous Solution on Activated Charcoal Powder

Parameters	Pseudo-first order	Pseudo-second order
Kinetics Constant	$K_1 = 0.0219\ min^{-1}$	$K_2 = 1.36 \times 10^{-3}$ g. mg^{-1}. min^{-1}
q_e (mg. g^{-1})	22.79	39.84
R^2	0.9538	0.9845
Adsorbent	Activated charcoal of Peanut shells	Activated charcoal of Peanut shells

CONCLUSION

Heavy metals abatement from wastewater has shown remarkable improvement using chemically modified biosorbent materials economically, without posing harm to the environment or biological systems. The

present research work concentrated on a readily available biosorbent for extracting Pb (II) ions from contaminated water sources by chemically modified activated charcoal powder derived from peanut shells with hydrochloric acid.

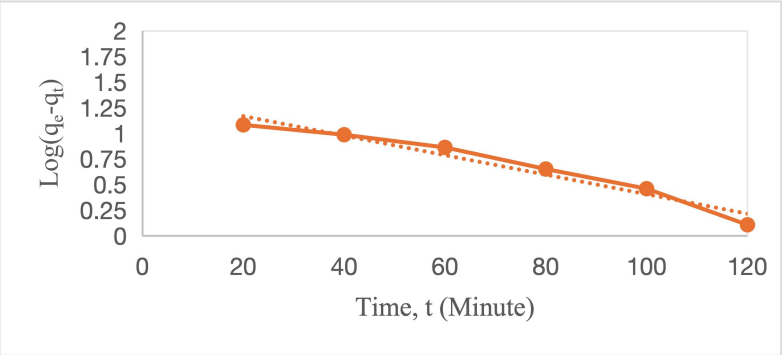

Fig.-6: Linearised Pseudo-first Order Plot

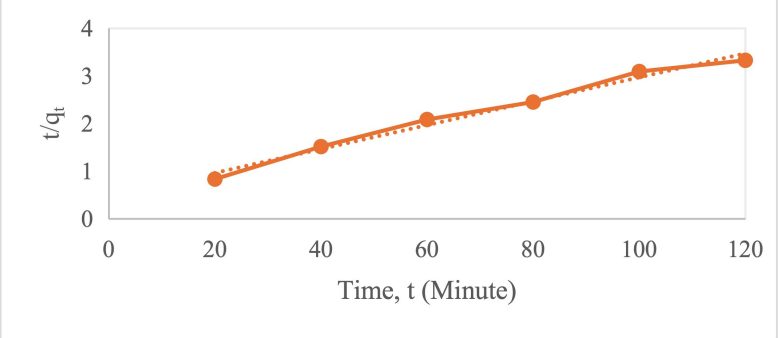

Fig.-7: Linearised Pseudo-Second Order Plot

The lead (II) ions uptake by activated charcoal derived from peanut shells has been successfully optimised under specific conditions. The findings of this study indicate that the maximum adsorption efficiency was achieved at a pH of 6, a contact time of 120 minutes, a biosorbent dosage of 1.5 g and 60 mg/L as the initial concentration of lead (II) ions. The maximum adsorption capacity was determined to be a value of 43.85 mg/g. The adsorption isotherms were substantially fitted with the Langmuir adsorption isotherm and the experimental data for kinetics modeling showed consistent alignment with pseudo-second order kinetics, indicating monolayer chemisorption on the adsorbent. These optimal conditions highlight the effectiveness of peanut shells activated charcoal as a readily available, economically viable and environmentally sustainable adsorbent for the abatement of lead (II) ions from contaminated water systems. The results demonstrate its effectiveness in wastewater treatment applications, particularly for heavy metals like Pb^{2+} ions remediation. Further studies may focus on the scalability, regeneration and real-world applicability of this biosorbent to enhance its practical utility in environmental remediation processes. Finally, chemically modified activated charcoal derived from peanut shells emerged as a promising and sustainable alternative for Pb (II) ions adsorption, contributing to the development of green technologies for pollution control.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6:Clean water and Sanitation*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

M. A. K. Azad https://orcid.org/0009-0003-6848-198X
M. A. Anwar https://orcid.org/0009-0009-5407-5706
R. Ranjan https://orcid.org/0009-0002-2277-7884

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