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Kinetic Model of Lead Adsorption by Raw and Carbonized *Ceratophyllum demersum*: Mechanisms and Rate Analysis

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Abstract: This work sought to examine the adsorption kinetics of lead (Pb^{2+}) ions on several types of Ceratophyllum demersum raw (CD), carbonized (CDCA), acid-activated (CDAC), and base-activated (CDBC). Graphs depicting lead adsorption over time indicate that the process occurs in two phases: an initial quick adsorption phase within the first few minutes (attributable to the availability of active sites), succeeded by a slow adsorption phase until equilibrium is attained. The adsorption process was examined by pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models to clarify the processes and rate-limiting phases. Batch tests were performed at temperatures between 20 and 35 °C, with Pb^{2+} concentrations quantified by Atomic Absorption Spectroscopy (AAS). The results indicated that the PSO model exhibited a superior fit (R^2 = 0.994–0.999) relative to the PFO model (R^2 = 0.981–0.988), suggesting that chemisorption is the predominant process. Base-activated carbon (CDBC) demonstrated superior adsorption efficiency due to increased surface functional groups. The results correspond with international research on biomass-derived adsorbents, validating the efficacy of C. demersum for sustainable wastewater treatment.

Keywords: Ceratophyllum demersum, Lead adsorption, Activated Carbon, Kinetic of adsorption, Adsorption activation energy

Introduction

Understanding adsorption kinetics is crucial for the design and optimization of effective systems for the removal of heavy metals, especially lead (Pb^{2+}), from contaminated water (Keskinkan, 2006). Lead is a persistent and toxic heavy metal that presents considerable environmental and public health risks due to its bioaccumulation and non-biodegradability (Taye et al., 2023) . Exposure to lead-contaminated water can result in neurological, renal, and developmental issues, particularly in children (Kumar et al., 2025). Consequently, the creation of affordable, environmentally sustainable, and high-efficiency adsorbents is an essential research focus in water treatment. Ceratophyllum demersum, a submerged aquatic plant prevalent in rivers and freshwater bodies in Iraq and other areas, has demonstrated significant potential as a precursor for activated carbon synthesis (Ghanim & Al-Mayah, 2020). The plant's composition is abundant in lignin, cellulose, and hemicellulose, rendering it appropriate for carbonization and chemical activation procedures that improve its porosity and surface functional groups (Duong et al., 2025). Equilibrium studies elucidate maximal adsorption capacity and surface contacts, whereas kinetic investigations disclose the rate of the adsorption process, the mechanisms involved, and the stages that constrain the process rate, this knowledge is crucial for extrapolating laboratory results to full-scale applications (Golabi et al., 2019). The kinetic analysis of heavy metal adsorption is essential for comprehending the adsorption mechanism and the rate-limiting factors. Pseudo-first-order (PFO) and pseudo-second-order (PSO) models are extensively employed to characterize adsorption behavior (Ho & McKay, 2000). Conversely, the PSO model posits that chemisorption is the predominant mechanism, characterized by valence forces resulting from the sharing or exchange of electrons between the adsorbent and adsorbate, and has demonstrated superior correlation

with experimental results in the majority of lead adsorption investigations (Tan et al., 2009; Wu et al., 2009) . Previous research have also included additional models, including the intraparticle diffusion (IPD) model and the Elovich equation, to elucidate diffusion control and surface heterogeneity in adsorption systems. Nonetheless, owing to its simplicity and superior accuracy, the PSO model continues to be one of the most efficacious instruments for analyzing kinetic data in batch adsorption systems (Çakman, 2024; Taye et al., 2023). This study synthesized four types of adsorbents derived from Ceratophyllum demersum raw (CD), carbonized (CDCA), acid-activated (CDAC), and base-activated (CDBC), used sulphuric acid and potassium hydroxide as activating agents. Batch adsorption tests were conducted under controlled conditions, and kinetic modelling was employed utilizing both PFO and PSO equations to assess the adsorption performance and infer the underlying process. Additionally, the Arrhenius equation was utilized to determine the activation energy (Ea) for each type of adsorbent, facilitating the differentiation between physical and chemical adsorption processes based on energy thresholds. This study seeks to assess the efficacy of Ceratophyllum demersum-derived adsorbents for the removal of Pb^{2+} and to juxtapose the results with current literature to determine the material's suitability for practical water treatment applications.

Experimental Part

Materials and Methods

The unprocessed Ceratophyllum demersum specimen was harvested from the Al-Diwaniyah River in Iraq, meticulously cleansed, sun-dried, pulverized, and sifted to achieve particle dimensions ranging from 150 to 300 µm. Four types of adsorbents were synthesized raw (CD), carbonized (CDCA), acid-activated (CDAC), and base-activated (CDBC). For carbonization, 50 g of CD were subjected to heating at 600 °C for 2 hours under a nitrogen gas flow of 60 mL/min. For chemical activation, 30 g of pre-carbonized CD were impregnated with 200 mL of 4 M H_2SO_4 or 4 M KOH solutions (carbon-to-solution ratio of 1:6.7 w/v), agitated for 30 minutes, and allowed to soak for 24 hours prior to drying. The impregnated samples were subsequently activated at 800 °C for one hour under nitrogen flow, rinsed with deionized water till achieving neutral pH, and dried at 200 °C. In adsorption tests, 0.1 g of each adsorbent was introduced to 100 mL of Pb^{2+} solution (20–100 ppm) and agitated at temperatures ranging from 20 to 35 °C. Samples were collected at designated intervals to assess adsorption kinetics utilizing a Shimadzu AA-7000 Atomic Absorption Spectrophotometer at a wavelength of 283.3 nm. The results were further evaluated by employing (PFO and PSO) kinetic models to ascertain the adsorption mechanism and rate.

Kinetic Model

- (PFO) Kinetics

The PFO kinetic model, first introduced by Lagergren in 1898, posits that the rate of adsorption site occupation is directly proportional to the quantity of empty sites. The model is often appropriate for physisorption, characterized by a relatively weak contact between the adsorbate and the adsorbent (Ho and McKay, 1999b). The linearized representation of the PFO equation is expressed as:

$$\log(q_e - q_t) = \log(q_e) - k_1/2.303 * t \qquad (1)$$

Where:
qt: amount of Pb^{2+} adsorbed at time (mg/g)
qe: adsorption capacity at equilibrium (mg/g)
k1: Rate constant (1/min)

This model is simplistic yet frequently inadequate in adequately representing systems that require chemical bonding or surface diffusion.

- PSO Kinetics

The PSO model, proposed by (Ho and McKay, 1999a), posits that adsorption adheres to a chemisorption mechanism, characterized by valence forces resulting from the sharing or exchange of electrons.
The linearized representation is:

$$\frac{t}{q_t} = \frac{1}{k_2 * q_e^2} + \frac{1}{q_e * t} \qquad (2)$$

Where:
K_2: second-order rate constant (g/mg·min)

This model typically provides a superior fit to experimental data compared to PFO, particularly where surface reaction constitutes the rate-limiting phase. It also facilitates a more precise calculation of equilibrium adsorption capacity.

Results and Discussion

Fitting of Kinetic Models

This study analyzed the adsorption kinetics of Pb^{2+} onto several adsorbents generated from Ceratophyllum demersum using two established models: the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models. These models were chosen for their simplicity, prevalence in adsorption research, and capacity to elucidate adsorption mechanisms. The PFO model, introduced by Lagergren, is generally linked to physical adsorption, positing that the rate of site occupation is proportional to the quantity of vacant sites. Conversely, the PSO model posits that chemisorption is the rate-limiting step, engaging valence forces via electron sharing or exchange between the adsorbent and adsorbate (Ho & McKay, 2000**;** Golabi et al., 2019)**.**

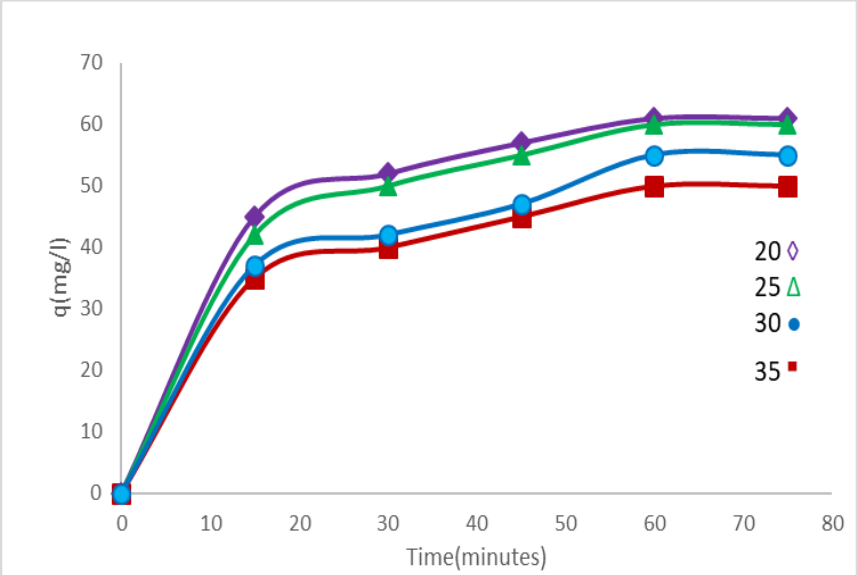

Figure 1. Rate of adsorption of Pb+2 on CD.

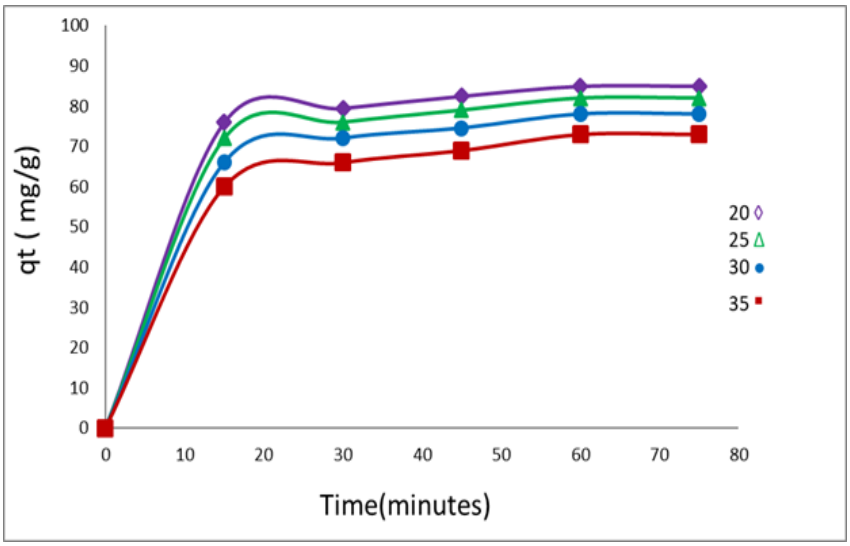

Figure 2. Rate of adsorption of Pb+2 on CDCA.

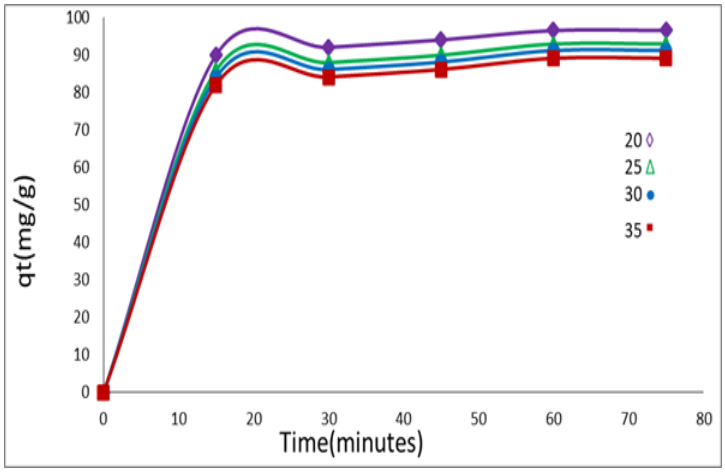

Figure 3. Rate of adsorption of Pb+2 on CDBC.

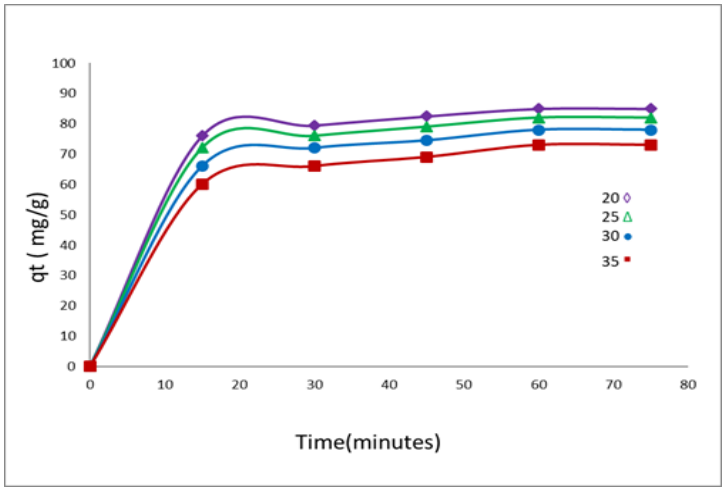

Figure 4. Rate of adsorption of Pb+2 on CDAC.

Figures 1 to 4 distinctly illustrate that lead adsorption transpires in two phases: an initial quick absorption within the first 15 minutes, attributed to the plethora of accessible active sites, succeeded by a gradual adsorption phase from 15 to 75 minutes as the active sites approach saturation. While more than 80% of the adsorption transpired during the initial rapid phase (0–15 min), only the subsequent period (15–75 min) was employed for kinetic model fitting. This choice was made to mitigate the impact of mass transfer resistance and external diffusion that prevail in the initial phase and diverge from the assumptions of these models. Concentrating on the second phase enables the models to more precisely delineate the intrinsic kinetics and rate-limiting stages related to the interaction between lead ions and the surface functional groups of the adsorbents.

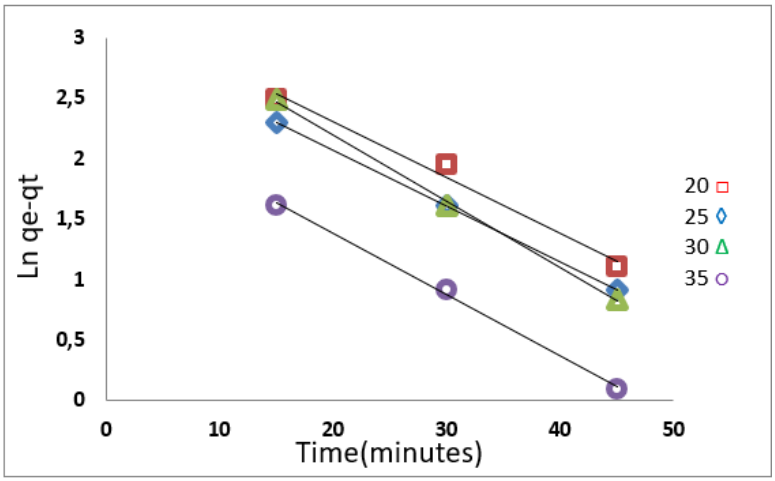

Figure 5. First order kinetic model for the adsorption of Pb on CD at different temperature

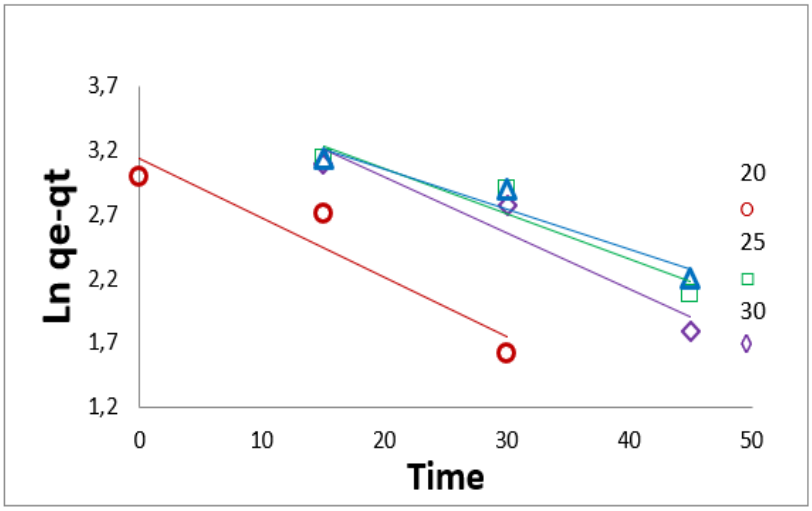

Figure 6. First order kinetic model for the adsorption of Pb on CDCA at different temperature

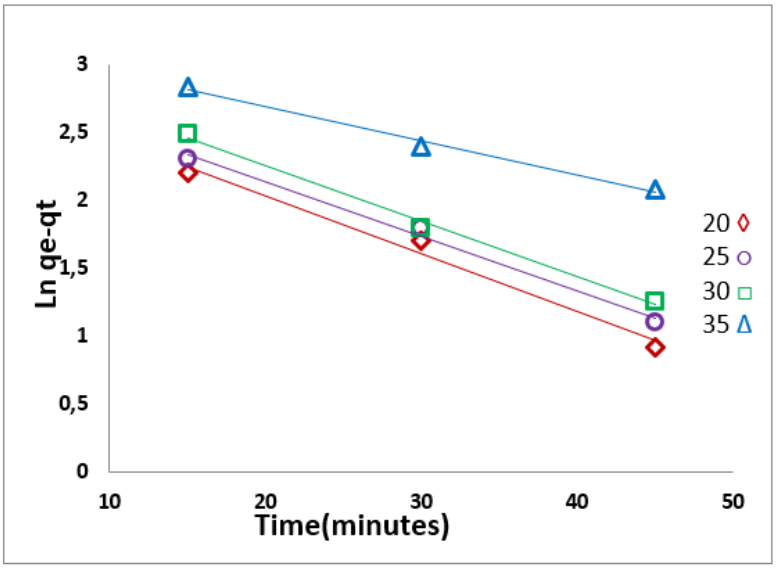

Figure 7. First order kinetic model for the adsorption of Pb on CDAC at different temperature

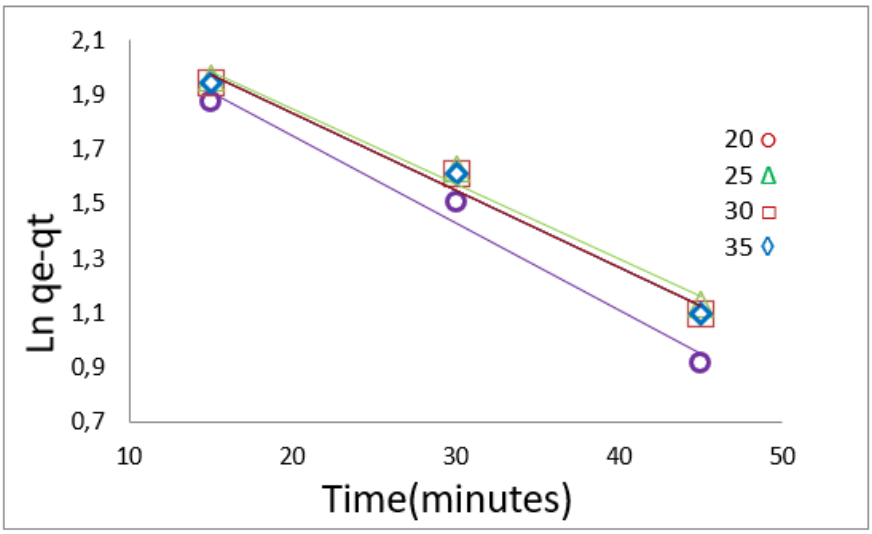

Figure 8. First order kinetic model for the adsorption of Pb on CDBC at different temperatures

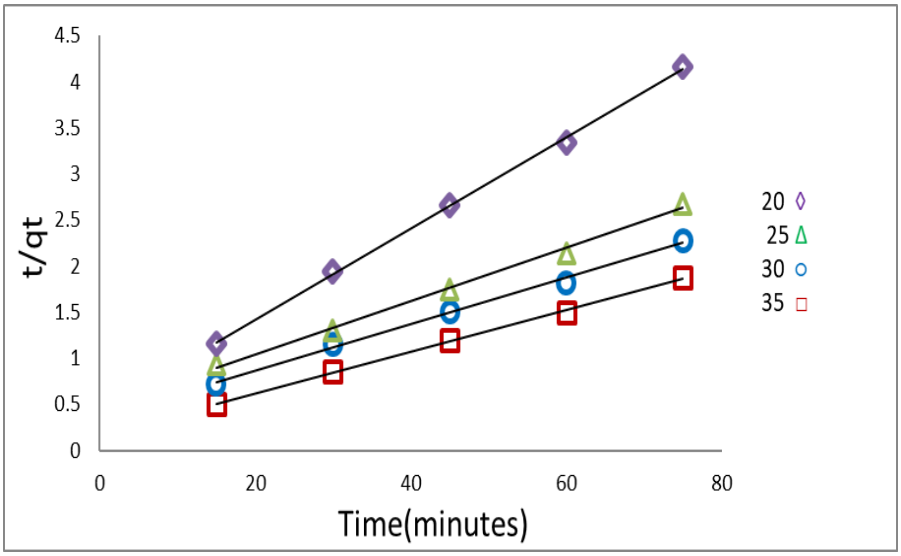

Figure 9. Second order kinetic model for the adsorption of Pb on CD at different temperature

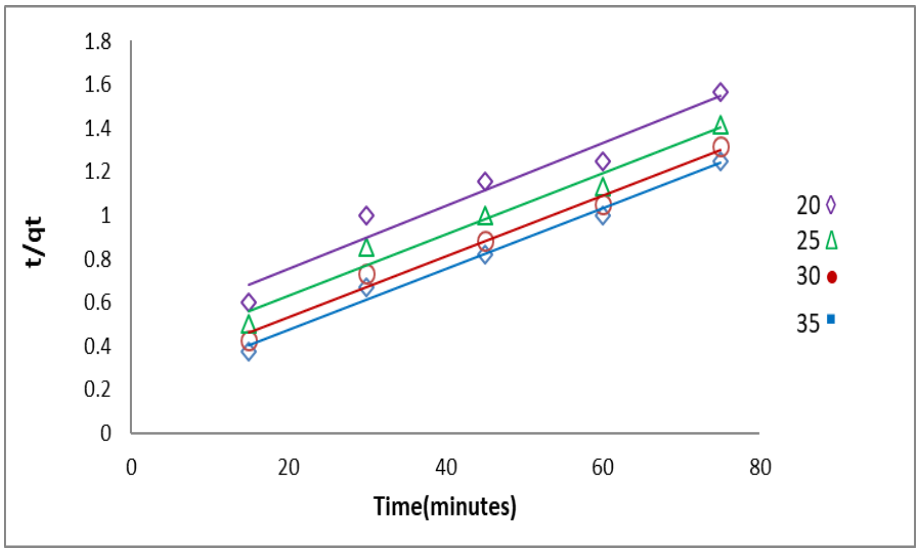

Figure 10. Second order kinetic model for the adsorption of Pb on CDCA at different temperature

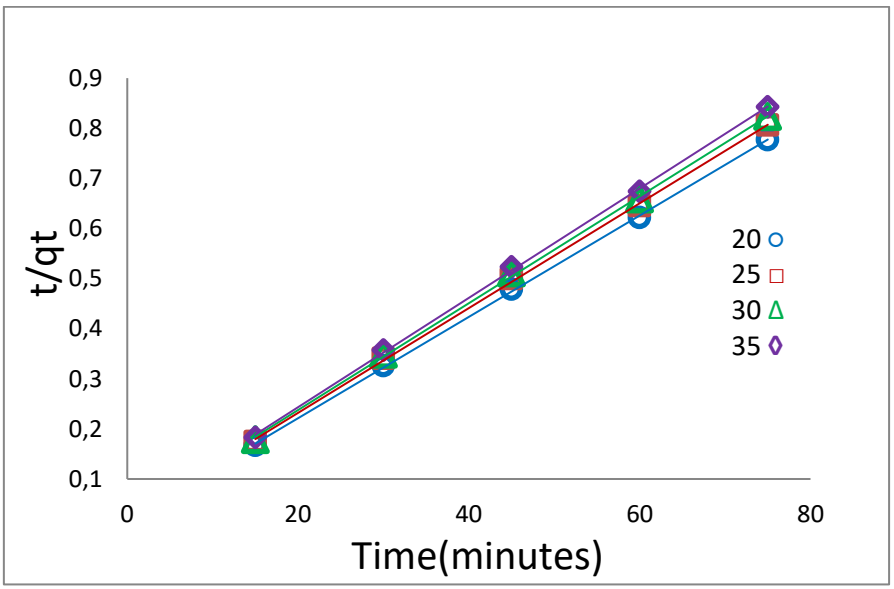

Figure 11. Second order kinetic model for the adsorption of Pb on CDBC at different temperature

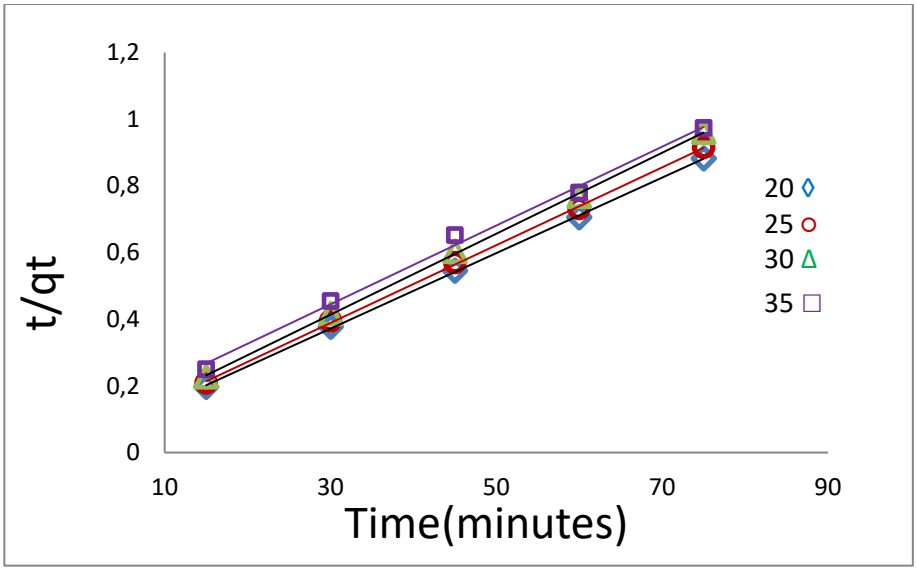

Figure 12. Second order kinetic model for the adsorption of Pb on CDAC at different temperature

From Figure 5 to 12, the data demonstrate that the PFO kinetics model is inconsistent with the experimental adsorption rate, while the PSO model accurately corresponds to the experimental adsorption rate. One can also observe how a PSO model represents experimental data by determining the confidence level (R^2) for the selected equations. The confidence level for pseudo second order models is 0.998, whereas the confidence level for PFO models is 0.987, indicating that the PSO model accurately represents the experimental data. Table 1 displays the PFO and PSO adsorption parameters for the adsorbate on the four types of prepared C. demersum at different temperatures. These findings correspond with prior study (Golabi *et al.*, 2019). They employed PFO and PSO models for the extraction of metals from wastewater. The conclusion was drawn that the PSO model sufficiently fits the data, exhibiting a R^2 value of 0.993. The kinetic analysis indicates that the adsorption of Pb^{2+} onto materials derived from Ceratophyllum demersum is driven by chemical interactions rather than mere physical diffusion, thereby underscoring the effectiveness of chemical activation and surface functionalization in improving adsorption performance.

Table 1. Average confidence interval levels (R2) for pseudo first order and pseudo second order.

Adsorbents	R2 Pseudo First Order	R2 Pseudo second order
CD	0.981	0.994
CDCA	0.983	0.995
CDAC	0.984	0.996
CDBC		0.999
0.988		

Table 1 indicated that the second-order kinetic model exhibited superior alignment with experimental data across all categories of adsorbents in comparison to the PFO model. The R^2 values in the PSO varied from 0.994 to 0.999, signifying that adsorption predominantly transpires via chemical interactions between lead ions and the functional groups on the adsorbent surfaces, particularly in the case of base-activated carbon, which exhibited the highest R^2 value of 0.999. The PFO model exhibited lower values, peaking at 0.988 for basic carbon, suggesting that physical adsorption alone insufficiently accounts for the system's behavior. The results affirm that the adsorption mechanism is mostly governed by chemical adsorption, aligning with the surface characteristics of the synthesized material and the elevated reactivity of its functional groups.

Model Comparison

The efficacy of the PSO model in characterizing Pb^{2+} adsorption has been thoroughly documented in the literature. Table 2 presents a comparative examination of kinetic performance to another analogous research.

Table 2. Comparison table of R^2 values for pseudo-first-order and pseudo-second-order models.

Adsorbent (Biomass source)	R2 Pseudo First Order	R2 Pseudo second order	Reference
Water Hyacinth (KOH-activated)	0.948	0.997	(Taye et al., 2023)
Activated carbon from seed coat of Euryale ferox	-------	0.997-0.99	(Kalita et al., 2017)
Euphorbia rigida –derived activated carbon	0.760	0.999	(Çakman, 2024)
Rice husk activated carbon	0.886	0.993	(Xu et al., 2024)

The results of recent studies presented in the table above demonstrate that the PSO kinetic model aligns more closely with experimental data than the PFO model, as evidenced by significantly higher R^2 values in all instances. This suggests that the adsorption mechanism in the majority of the utilized plant materials primarily relies on the chemical interactions between lead ions and the active functional groups on the surface of the activated carbon, including hydroxyl and carboxyl groups. The results demonstrate a clear alignment with the study's findings, as the adsorbents derived from the C.demersum plant, particularly the base-activated carbon, exhibited superior performance when evaluated using the second-order model. This reinforces the hypothesis that the lead removal mechanism is predominantly governed by chemical adsorption rather than merely physical processes and substantiates the viability of utilizing this plant material in environmental remediation efforts, achieving effectiveness comparable to other globally tested materials in recent studies.

Activation Energy

The activation energy (Ea) denotes the minimum energy threshold that must be surmounted for the adsorption process to occur. In the context of eliminating heavy metals such as lead (Pb^{2+}) from water via biomass-derived carbon adsorbents, Ea is crucial in ascertaining the predominant adsorption process. Lower (Ea) values (often < 40 kJ/mol) signify physisorption, predominantly influenced by weak forces such van der Waals interactions. Conversely, elevated (Ea) values (> 40 kJ/mol) indicate chemisorption, characterized by robust chemical bonding between the adsorbate and the adsorbent. To determine Ea for each variant of Ceratophyllum demersum-derived adsorbent, the Arrhenius equation was utilized in its linearized format 3 (Ho and McKay, 2000):

$$\text{Ln}\,(k) = \ln(A) - Ea/RT \qquad (3)$$

Where:
K: the PSO rate constant (g/mg·min)
A: the Arrhenius pre-exponential factor
R: the universal gas constant (8.314 J/mol·K)
T: the absolute temperature in Kelvin
Ea: the activation energy (J/mol)

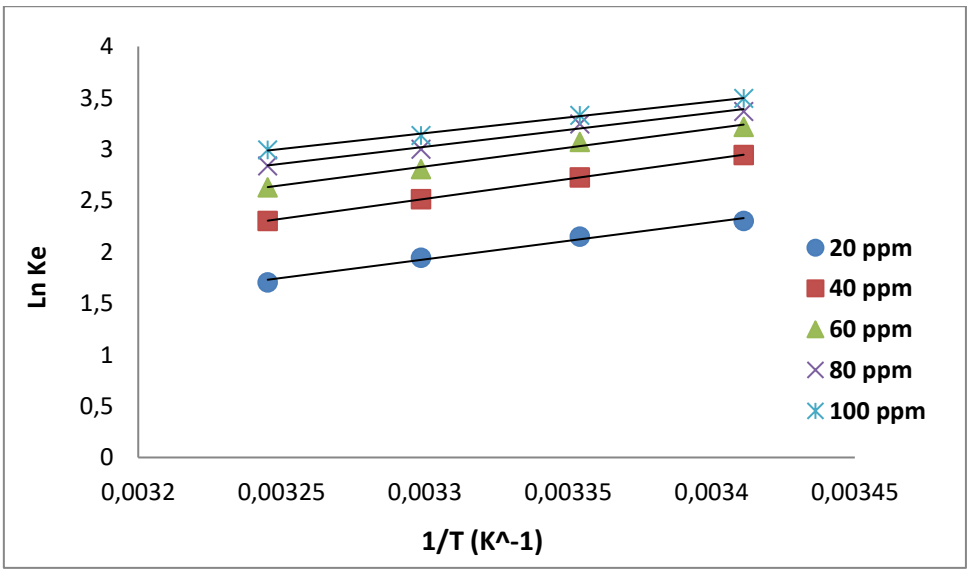

Figure 13. Arrhenius plot of versus for Pb^{2+} adsorption onto raw ceratophyllum demersum (CD).

By plotting ln K2 versus 1/T for each adsorbent, a linear relationship is established, and the slope (–Ea/R) facilitates the determination of Ea. The subsequent figures display the Arrhenius plots and computed activation energies for each adsorbent. The graph 13 illustrates the Arrhenius relationship for the adsorption of lead (Pb^{2+}) ions utilizing raw Champlain plant as a natural adsorbent. The correlation between the natural logarithm of the equilibrium constant (Ln Ke) and the reciprocal of the absolute temperature (1/T) was graphed for various beginning concentrations (20–100 ppm). The graph illustrates a linear correlation, suggesting that the adsorption behavior aligns with the Arrhenius model. The activation energy for the process was determined to be 17.401 kJ/mol from the slope of the straight line. This figure signifies that the adsorption process is primarily physical, given that physical activation energies are often below 40 kJ/mol. This outcome verifies that adsorption transpires swiftly without necessitating the rupture of robust chemical bonds, hence augmenting the efficacy of raw Champlain plant as an economical and efficient adsorbent for the remediation of lead-contaminated water, particularly at ambient temperatures.

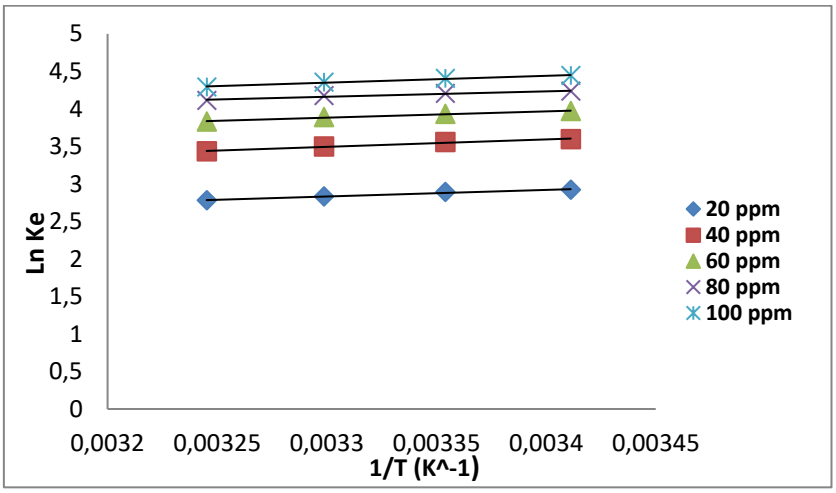

Figure 14. Arrhenius plot of versus for Pb^{2+} adsorption onto carbonized (CDCA).

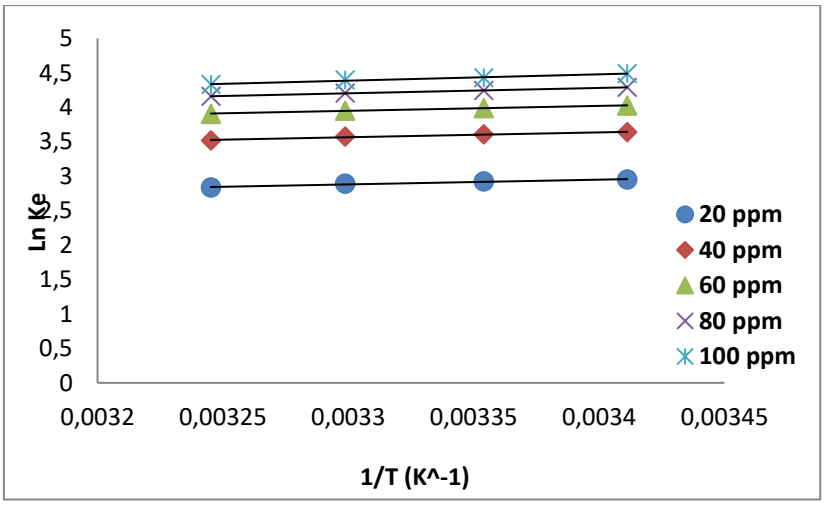

Figure 15. Arrhenius plot of versus for Pb^{2+} adsorption onto acid-activated (CDAC).

Figure 14 depicts the correlation between the natural logarithm of the equilibrium constant (Ln Ke) and the reciprocal of absolute temperature (1/T) for varying initial concentrations of lead ions (Pb^{2+}) utilizing inactivated carbon derived from the CD plant as an adsorbent. The graph exhibits a distinct linear relationship across all concentrations (20–100 ppm), signifying that the system adheres to the Arrhenius model. The slope of the resultant straight line yielded an activation energy (Ea) of 30.42 kJ/mol for the process. This value suggests that the adsorption is physical, as it lies within the standard range for physical adsorption (< 40 kJ/mol). This signifies that the adsorption process does not necessitate the cleavage of robust chemical bonds, but instead depends on van der Waals forces or electrostatic attraction, illustrating the swift and reversible character of the interaction between lead ions and the inactivated carbon surface. Inactivated carbon offers an adequate active surface for effective lead ion adsorption; nevertheless, its process is less efficient than that of activated carbon, perhaps due to its restricted porosity and fewer active sites.

Figure 15 above shows the Arrhenius type plot between Ln (K_e) and 1/T (K^{-1}) of the acid prepared AC, from Champlain plant, in different concentration lead ion (Pb^{2+}). It was observed that the plots show a linear hyperbolic behavior of ln (K_e) against 1/T at all concentrations (20, 40, 60, and >80 ppm), illustrating the fact that adsorption generally follows Arrhenius behaviour. The increase of ln (K e) with increase in temperature (decrease in 1/T) indicates that the adsorption process is endothermic. The activation energy (Ea) obtained from the gradient of the linear plots was 25.01 kJ/mol, indicating that the adsorption process is essentially physical with probably some superficial chemical reaction. Such a response suggests that the (CD)-activated carbon is efficient in removing lead ions from an aqueous medium even in wide temperature range.

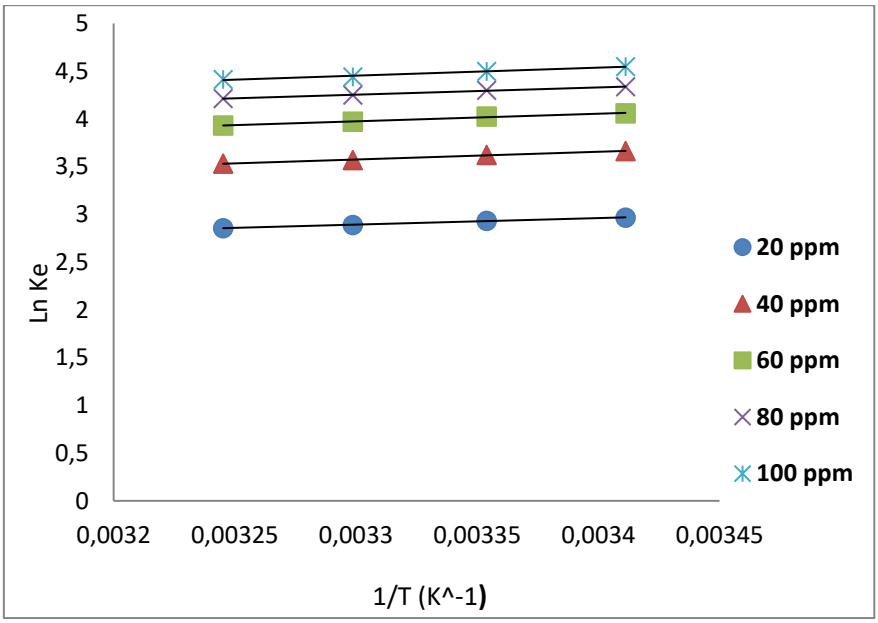

Figure 16. Arrhenius plot of versus for Pb^{2+} adsorption onto (CDBC).

Graph 16 ln (Ke) Vs Timperature paramater of Arrhenius equation for activated carbon prepared by Potassium hydroxide (KOH) treated CD plant. A strong positive linear relationship is observed between them which confirm that the adsorption follows Arrhenius type behavior. The positive rise is indicative of an endothermic adsorption process and the increasing temperature favours higher efficiency in the adsorbent. The activation energy (Ea) for this reaction was 33.291 kJ/mol, indicative of physical adsorption process with weak van der Waals forces and electrostatic interactions as the main adsorption mechanisms combined with possible secondary surface reactions. This phenomenon was attributed to the unique properties of base-activated carbon with a large surface area and microporous nature, which makes it an effective adsorbent over a wide temperature range. The reversible nature of the physical adsorption of C on carbon, suggests that the adsorbents can be reused after regeneration processes, which would enhance its application in environmental purification and Waters processing.

Conclusion

Kinetic studies of Pb^{2+} adsorption on the adsorbents developed from Ceratophyllum demersum showed that pseudo-second-order (PSO) model was more effective for adequate fit of the experimental data with a squared regression coefficient R^2 ranging between 0.994 and 0.999, thus indicating chemisorption as an endothermic process. Over 80% of lead removal occurred within the first 15 min, signifying an extremely efficient adsorption process. CDBC was identified as the best performing adsorbent in all synthesized adsorbents with maximum Q m of 179 mg/g and R^2 of 0.999. This enhanced performance can be attributed to the increased surface functionalization and microporosity from KOH activation. Use of the Arrhenius equation further confirmed the translation from a physical to chemical adsorption behavior. These results promote C. demersum-activated carbon based on CDBC as an efficient, low-cost and environmental-friendly extractor for heavy metals from contaminated water. Further studies should focus on the regeneration of adsorbent, treating actual wastewater and adsorption in multi-metal systems to estimate its practical applicability at large scale.

Recommendations:

- Examine the viability of reusing the adsorbent over several cycles.
- Conduct performance testing on authentic multi-metal contaminated water instead of solely on industrial solutions.
- Perform an extensive economic assessment to illustrate the viability of utilizing activated carbon from Ceratophyllum in large-scale water treatment processes.

Scientific Ethics Declaration

* The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Conflict of Interest

* The authors declare that they have no conflicts of interest

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