Machine Learning-Augmented Real-Time Prediction and Analysis of Lead Adsorption Behaviour at Different Temperatures

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Abstract
Contamination of drinking water sources with lead is one of the most significant environmental and public health problems and, consequently, highly efficient absorption-based elimination strategies are highly sought after. Here, a machine-driven real-time lead adsorption behavior for a series of temperatures is reported based on modeling of the adsorption isotherm models. The experimental data is reproduced, followed by the development of a novel prospective predictive framework. Mechanism of adsorption was screened over various parameters: concentration of adsorbent (10–60 mg/L), pH (4–9), contact time (30–180 min), adsorbent meal load (1–6 g/L) and temperature (100 °C, 150 °C, 200 °C) in a bid to determine their effect on adsorption effectiveness. Three isotherm equations, namely Dubinin–Radushkevich (D-R), Redlich–Peterson (RP) and Sips, were used to solve the adsorption process. The model that fits the experimental data better i.e. Sips model with the highest R^2 value (R^2 0.9995), was selected here, as the nearest fit.

In order to improve the real-time predictive accuracy, a Random Forest Regressor (RFR) model was constructed with experimental data and resultant highest prediction accuracy (Mean Squared Error (MSE) 0.00009, Root Mean Squared Error (RMSE) 0.00937, R^2 0.97513). These results validate the applicability of the model to predict adsorption of a set of experimental conditions.

Results show that the highest adsorption yield occurs under the elevated temperature, optimal pH environment and longer contact time, while excess adsorbent dosing causes adsorption saturation effect and decreases the adsorption enhancement. In this study, the feasibility of machine learning assisted adsorption modelling for optimization of the real-time water treatment processes is shown.

Keywords: Lead removal, Machine learning supported modeling, Adsorption isotherms, Sips shaped isotherm, Predictive analysis, Adsorption capability, Heavy metal adsorption, Adsorption efficiency, Environmental remediation, Water treatment methods.

Introduction

Water contamination from industrial sources involving mining, battery manufacture and electroplating with lead, is a serious environmental and public health threat as toxic effects even at low exposure can occur. Health risks include neurological deficits, developmental retardation, renal failure and cardiovascular disease[10]. Adsorption is a strong suit when developing a lead removal system, as it is intrinsically simple, cheap and adsorbent recyclable. Typical adsorbents studied are activated carbon, biochar, metal-organic framework (MOF) and nanomaterials[2]. Limitations in adsorption performance due to pH, contact time, adsorbent dosage and temperature are also discussed. Despite their time-consumption and their potential static nature, traditional batch experiments are commonly applied to study adsorption behavior.

Lead Contamination in Water and Environmental Consequences: Water pollution with lead (Pb) is an important environmental and public health problem globally. Because of its non-degradable and high toxicity, lead is polluting water resources and creates serious threats to aquatic environment and the surrounding human population. Major sources of lead contamination are industrial discharges, mining, battery assembly, plumbing systems made of lead piping and improper elimination of electronic waste[15]. Lead may contaminate water bodies by way of leaching from corroded pipes, industrial discharges and atmospheric deposition from combustion of fossil fuels. Because the repeated exposure to lead in drinking water is known to have serious health consequences even at low doses, its presence in drinking water is becoming especially problematic. Lead poisoning leads to cascading effects in aquatic and earthbound ecosystems. Lead water poisoning effects are, mainly, presented as follows:

- **Impact on Aquatic Life:** Lead ions impair the physiological mechanism of aquatic organisms through enzyme inactivation and modulation of cellular metabolism. Bioaccumulation in fish may culminate in reproductive failure, behavioral alteration, higher mortality and haemoglobin disaggregation resulting in reduced oxygen uptake.
- **Soil and Sediment Contamination:** Lead accumulates as part of sediments and can stay there for centuries and serves as a hidden form of pollution when returning to the water body as a result of environmental events. Contaminated soils with lead negatively affect microbial diversity and plant growth, thus affecting agricultural production[10].

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- **Bioaccumulation and Biomagnification:** Lead dorsally is concentrated through the food chain at various trophic levels and, as a result, toxicity increases in its predators. This poses serious risk to birds, mammals and humans consuming contaminated fishes or agricultural commodities. Lead's mobility and toxicity are affected by pH, temperature and dissolved organic matter[2].
- **Public Health Risks:** Lead exposure via drinking water is one of the most prevalent epidemiologic manifestations of human lead poisoning and of the utmost concern in areas of ageing infrastructure. Persistent subjection is prone to neurological, cardiovascular and kidney damage. Infants and pregnant women particularly at risk, for developmental and for chronic cognitive decline[10].

Water contamination with heavy metals is an ecological and public health disaster that calls for efficient remediation measures. Common classical techniques, like chemical precipitation, ion exchange and membrane filtration, are widely applied, but the suggested methods are relatively expensive along with generation of secondary waste and low throughput at low levels of lead. Adsorption is known as low cost and environmentally benign. The efficiency is affected by the parameters such as temperature, pH, contact time and property of adsorbent.

In order to improve the adsorption performance and to optimize the process, the machine learning combined with experimental adsorption, an attractive strategy, is proposed. This synergism allows for *in situ* analysis, modeling and better decision-making in sustainable water purification.

Existing Methods of Lead Removal and Their Limitations: Waterborne lead pollution creates a serious environmental and public health issue because of its toxicity persistence. Different traditional and modern treatment techniques have been invented to remove the lead from contaminated water supplies. Although such methods have different extents of successful operation, they each represent method with intrinsic limitations preventing their big scale use.

- **Chemical Precipitation:** Chemical precipitation is one of the most widely used methods for lead removal from wastewater. It involves adding chemical agents such as hydroxides, sulfates, carbonates, or sulfides to facilitate the formation of insoluble lead compounds which can then be separated through sedimentation or filtration[5].
- **Ion Exchange:** Ion exchange is realized through the use of resin-based materials which exchanges lead ions for less toxic ions e.g. sodium (Na^+) or hydrogen (H^+) in a reversible reaction[3]. This method is effective for removing lead from both drinking water and industrial effluents.
- **Membrane Filtration (Reverse Osmosis, Nanofiltration, Ultrafiltration):** Membrane filtration techniques including reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF), use semi-permeable membranes to physically separate lead ions from water based on molecular size and charge.
- **Electrocoagulation:** Electrocoagulation (EC) employs an electric current to dissolve metal electrodes (e.g. aluminium or iron), releasing coagulants that bind with lead ions to form precipitates that can be removed via sedimentation or filtration.
- **Adsorption (Activated Carbon, Biochar, Nanomaterials, Zeolites):** Adsorption is a widely used technique where lead ions bind to porous materials such as activated carbon, biochar, zeolites, or nanomaterials through physical or chemical interactions[2].
- **Bioremediation (Microbial and Phytoremediation Techniques):** Bioremediation involves using microorganisms (bacteria, fungi, algae) and plants to absorb, bioaccumulate, or transform lead into less toxic forms.

Each lead removal method has advantages and challenges, necessitating careful selection based on water composition, cost considerations and environmental impact. Traditional methods are effective but suffer from high operational costs, sludge generation and maintenance issues. Adsorption and bioremediation offer promising eco-friendly alternatives but require optimization for large-scale applications.

Importance of Adsorption-Based Methods using Biomass Materials for Lead Removal: Water lead contamination is an important environmental and public health concern because of the toxicity and bio-accumulation of lead. The most widely used physicochemical techniques for the removal of lead, chemical precipitation, ion exchange and membrane filtration, are all costly, energy demanding and produce municipal wastes. Adsorption has found increasing appeal as an effective and low-gold-cost alternative, simple to operate with high removal performance. Specifically, biomass-derived adsorbents that are synthesized from agricultural and industrial waste products have also attracted considerable interest as they offer a range of sustainability, utility and high adsorption abilities[2, 3]. The types of biomass-based adsorbents for lead removal are agricultural waste-derived adsorbents, microbes (such as algae, fungi and bacteria) and biochar-based adsorbents.

Research Gaps in Biomass Adsorption for Lead Removal: More and more researches are available for adsorptive removal of Pb from biomass-derived strategies, but the result in terms of slow kinetics of adsorption, poor regeneration ability and different performance according to the environmental conditions must be considered for the industrial application. Given field variability and the absence of information for continuous flow systems as a background, translation is a barrier. There is a potential application of machine learning (ML) also in conversion technologies which can offer high added value, such as high-performance design of adsorption parameters, deep data analytics or real-time process control and so on. The algorithms of artificial neural networks (ANNs), support vector machines (SVMs) and decision tree models have also been used to make prediction of adsorption capacity, selection of appropriate biomass materials and optimization of basic parameters i.e. pH, contact time and temperature.

Biomass-derived adsorbents obtained for lead removal property from agro-industrial biomass, microbial biomass and biochar are promising from an economic and environmental point of view. Nevertheless, chemical derivatization and machine-learning (ML)-driven optimization are still required to still enhance performance. When used together with biomass, functionalized nanoparticles and mesoporous composites adsorbents are provided to improve the adsorption performance. ML can also be used in predictive modeling and real time monitoring and cost reduction and therefore, would help to reduce the need for high throughput laboratory tests. The integration of experimental know-how in ML-driven prediction, therefore, can result in efficient, green and workable lead removal water treatment (WLWT) technologies.

The general objective of this work is to implement an ML-based framework for real-time analysis and optimization of the lead adsorption behaviour at different temperatures. When investigating the system, data driven modeling approaches are applied to predict adsorption behaviour, to define thermodynamic behaviour and to regulate the process.

- **Analyzing Temperature Influence:** Temperature changes on lead adsorption capacity, kinetics and thermodynamics are compared.
- **Developing ML-based Prediction Models:** Implement data driven models for the prediction of adsorption efficiency based on experimental data.
- **Evaluating Adsorption Kinetics and Isotherms:** Empirical models and data supported models are used for characterization of adsorption mechanisms.
- **Real-Time Monitoring and Optimization:** Develop an imbalanced learning-based, real-time absorption efficiency forecasting and process control system.

In this study, an algorithm application-based machine learning for real-time prediction and temperature-dependent lead adsorption behaviour analysis and deep optimum is proposed. The purpose of the current study is to maximize decision making, performances and scalability of the adsorption-based aqueous water treatment processes, that can be applied toward the development of even sustainable lead-remediation technologies. Results of this work can be applied to intelligent water treatment systems that include ML-based decision making to maximize adsorption capacity and environmental pollution.

In this study, aiming to reverse the separation between the experimental adsorption performance of removal of lead in real time application and computational intelligence, this research aims to remove this gap between experimental adsorption work and computational intelligence.

Review of Literature

Contamination of drinking water by lead is a serious environmental, public health threat and even low-level exposure is associated with neurologic disease, renal dysfunction and congenital malformation. Highly effective lead removal has been a decisive step in promoting water safety and, in this context, adsorption has been recognized to be an attractive low-cost removal method, mainly due to its ease of implementation, high removal efficiency and material recyclability. Nevertheless, adsorption performance is influenced by temperature, pH, initial Pb concentration and adsorbents properties. Old adsorption isotherm techniques are not valid in predicting *in situ* properties based on real-time measurements for dynamic systems. The combination of machine learning (ML) and the adsorption process is a promising date for real time prediction, optimization of adsorption performance and minimization of the need for conventional laboratory tests, improving the lead removal efficiency and treatment performance respectively.

Tchounwou et al[10] provided an extensive account of environmental distribution, human exposure pathways, toxicity mechanisms and carcinogenic risk of five priority heavy metals arsenic, cadmium, chromium, lead and mercury. These metals are the known as systemic toxicants which exert damaging health effects, including organ damage and cancer at low exposure levels. An average of more than 100,000 (and sometimes millions) persons in Bangladesh/India are chronically exposed to arsenic in drinking water. There is wicking of lead contamination in 25% of US homes with young child. Babel and Kurniawan[2] discussed the potential of several inexpensive adsorbents as substitutes to activated carbon for the removal of heavy metal from polluted water.

High adsorption abilities are realized by natural materials (chitosan, zeolites, clays and industrial by-products - waste slurry, lignin and red mud). Key findings indicate that chitosan adsorbs 815 mg/g of Hg^{2+}, 273 mg/g of Cr^{6+} and 250 mg/g of Cd^{2+} whereas zeolites remove 175 mg/g of Pb^{2+} and 137 mg/g of Cd^{2+}. Industrial waste-derived adsorbents including waste slurry are extremely effective, showing adsorption capacities up to 1030 mg/g for Pb^{2+} and 560, 640 mg/g for Hg^{2+} and Cr^{6+} respectively. Lignin exhibits the highest Pb^{2+} removal at 1865 mg/g.

Tran et al[11] also critically reviewed conflicting findings in adsorption and pointed the importance of precise measuring, mathematical modeling and data interpretation. Major findings demonstrate that adsorption performance should be expressed with equilibrium adsorption capacity instead of percentage removal to avoid ambiguity. Zhang et al[14] studied the detection and removal of moderate high concentration of tetracycline (TC) in aqueous solution using multi-walled carbon nanotubes (MWCNTs) as adsorbents. The adsorption efficiency reached 99.8%, demonstrating MWCNTs' performance. Zhao et al[15] used machine learning for the prediction of the adsorption capacity of organic molecules adsorbed on biochar and polymeric resins. Using 1750 adsorption data points of 73 organic substances, the model performed significantly superior (R^2 0.940 and 0.976 compared to NN-LFER-based models) (R^2 0.870 and 0.880 respectively) in predictions on biochar and resin.

Flora et al[4] also studied the lead (Pb) toxicity and its biological damage effects in particular with regard to the involvement of oxidative stress. Subacute/chronic lead toxicity, characterized by persistent vomiting, encephalopathy and convulsions and diagnosed based on the blood lead levels of 40–60 µg/dL. Jaishankar et al[6] studied toxicity, mechanisms health effects of heavy metals and proposed their role in human US environment pollution. Wuana and Okieimen[13] described the cause, chemical, hazard and remediation soil contaminated environment by soil contamination.

Phytoremediation alters as an eco-friendly option but requires long-term monitoring. Technical brief[12] described lead contamination in drinking water and potential health hazards and the requirement for permanent monitoring and remediation. According to the World Health Organization (WHO)[12], lead concentrations should be below 10 µg/L because exposure has been shown to be associated with cognitive deficits, especially in children.

Needleman[8] further described the effects of lead poisoning on the human health, particularly regarding the neurological, renal and the hematopoietic system. Chronic exposures also have been inter-linked to cognitive and behavioral dysfunction as well as cardiovascular disease even at low doses. Fu and Wang[5] estimated numerous methodologies to remove heavy metal ions from wastewater, focusing on their efficiency and practical applicability. The adsorption with activated carbon and bio sorbents is proved effective and the adsorption capacity which is more than 99% for lead and copper, is obtained. Barakat[3] provided a review of recent method for the treatment of industrial effluents contaminated with heavy metals that include some novel physicochemical methods.

Adsorption using newly developed adsorbents and membrane filtration are two of the most investigated and applied methods with high capacities of removal. Alyüz and Veli[1] studied the adsorption of nickel and zinc from aqueous solution on Dowex HCR S/S cation exchange resin. Batch adsorption experiments were used to show that the maximum percentages of nickel and zinc adsorption were obtained at pH 4 and 6 respectively with more than 98% removal percentages. Kansaraa et al[7] discussed different methods for lead removal from wastewater, particularly considering adsorption, ion exchange, precipitation and membrane filtration.

Removal efficiencies have been shown to be higher than 95% for adsorption using activated carbon and bio-sorbents, as the result of widespread studies. Highly selective for Pb^{2+} ions, ion exchange resins like zeolites adsorb Pb^{2+}ion at over 150 mg/g. Ngah and Hanafiah[9] surveyed the application of chemically functionalized plant waste as an inexpensive absorbent for the removal of heavy metal ions from wastewater. Chemically modified plant-based materials, such as rice husk, sawdust and sugarcane bagasse, have very improved adsorption capacities in comparison to the unmodified ones.

The use of nanomaterials, biochar, bio-sorbents or agricultural waste is proven in recent researches for heavy metal and dye removal from wastewater. These materials are very high in adsorption capacity, low in cost and environmentally acceptable, therefore it is feasible to replace conventional treatments. Operationally, chemically modified biochar, magnetic nanocomposites and used adsorbents, all demonstrate elevated adsorption capacity due to increased surface area and reactivity. However, problems still exist in the applications at large scale, the long-term performance and the regeneration capability. There is a need for future research to further adjust the characteristics of adsorbents, strengthen recyclability and embed these materials into an integrated wastewater treatment system to increase its efficiency and scaling properties to provide pollution control.

Material and Methods

A real time machine-learning-based predictive system based on lead adsorption modelling has been described to predict adsorption at various temperatures. The study reports adsorption kinetics, equilibrium determination and thermodynamics, over a temperature range. Integrated experimentation with optimized adsorbents and ML models was utilized to examine the adsorption efficacy and predict the system performance. In the methodology, data pre-processing, feature selection and model training are performed to enhance the performance of the model. In the current method, a thermodynamically consistent method is presented for mapping lead adsorption kinetics which in turn, is used to guide process optimization and increase removal efficiency.

Adsorbent Preparation and Characterization

Biomass-Based Adsorbents: The current work investigates rubber seed shells, tamarind pod shells, groundnut shells and Pistachio shells as low-cost/green adsorbents for removal of heavy metal(s). These abandoned, agricultural waste biomass materials which contain a high carbon content, have high porosity and have a large number of surface functional groups which are good candidates for adsorption.

- **Rubber Seed Shells (RSS):** Composed of cellulose (35–40%, hemicellulose (20–25% and lignin (30–35%, rubber seed shells lend a stable structure to adsorption. Their surface can be chemically functionalized in order to improve binding of heavy metal ion.
- **Tamarind Pod Shells (TPS):** Highly enriched in cellulose (40-45% and lignin (25-30% with polar

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functional groups, including carboxyl -COOH) and hydroxyl -OH). Metal ion interaction capability has been enhanced.

- **Groundnut Shells (GS):** Groundnut shells are composed with lignocellulosic basis of cellulose (35–45%, hemicellulose (20–25% and lignin (30–35% have 50% moisture content, their architecture is inherently porous and hence highly effective in adsorption efficiency.
- **Pistachio Shells (PS):** Pistachio shell, being a natural heterogeneous material composed of 40–50% cellulose (40–50%, 20–25% hemicellulose (20–25% and 25–30% lignin (25–30%, possesses a naturally coarse surface that enhances the adsorption characteristics of the shells.

Adsorbent Preparation: Each biomass material underwent a systematic preparation process to enhance its adsorption properties:

- **Washing and Drying:** Raw materials were washed with distilled water repeatedly to wash out impurities and oven dried at 105°C for 24 h.
- **Grinding and Sieving:** Dried biomass was milled and sieved to provide particles of 100–500 µm.
- **Carbonization and Activation:** Activated carbon was prepared from the biomass pyrolyzed in 400–700 °C temperature range *in vitro* under nitrogen atmosphere in a Muffle furnace. Chemical activation using H_3PO_4 or KOH was performed to increase pore volume and increase surface area.

Experimental Setup for Lead Adsorption: To explore the adsorption behavior of lead ions (Pb(II) at elevated temperatures, batch adsorption experiments were carried out at 100°C, 150°C and 200°C at the laboratory level under the same conditions. The study focused on evaluating the adsorption efficiency, measuring initial and final lead concentrations and determining the adsorption capacity of the prepared adsorbents.

- **Adsorption Experiment Setup:** The adsorption experiments were performed using 250 mL stoppered glass bottles, where the intended mass of each adsorbent was combined with 50 mL of Pb(II) solution at predefined temperatures. A thermostatically controlled water bath shaker was employed to keep the experiment temperature constant and the process of adsorption kinetics equal across the experiment. Adsorbate-adsorbent interaction was maximized by continuously mixing the solution at a pre-determined rate.
- **Temperature-Dependent Adsorption Studies:** To compare the impact of temperature on lead adsorption, experiments were performed at various temperatures. At 100°C (373 K), performance of the early stage of the temperature effect on adsorption behavior at 150°C (423 K) was evaluated for intermediate thermal effects and putative structural modifications in the adsorbent and at 200°C (473 K), high-temperature effects increased diffusion and possible adsorbent deactivation may occur. Experimental protocols were identical for each temperature condition in order to make the experiment reproducible.
- **Measurement of Initial and Final Lead Concentrations:** Before and after, adsorption absorbance of Pb(II) in the solution was measured by an Atomic Absorption Spectrophotometer (AAS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) in order to achieve accurate quantification. The steps involved were:
    - **Initial Concentration (Co) Measurement:** Pb(II) solutions of known concentrations were prepared and analyzed before adsorption.
    - **Filtration:** After the specified shaking time, the adsorbent was separated from the solution using a 0.45 µm membrane filter.
    - **Final Concentration (Ce) Measurement:** The remaining Pb(II) concentration in the supernatant was determined post-adsorption.
- **Adsorption Capacity Calculation:** The adsorbent's adsorption capacity per gram of adsorbent at equilibrium Q_e was determined by using the mass balance equation:

$$Q_e = \frac{c_0 - c_e}{m} * V$$

where Q_e is Adsorption capacity (mg/g), C_o is Initial Pb(II) concentration (mg/L), C_e is Equilibrium Pb(II) concentration (mg/L), V is Volume of Pb(II) solution (L) and m is Mass of the adsorbent (g).

- **Adsorption Efficiency Calculation:** The overall removal efficiency (R_{eff}) of the adsorbent was calculated using the following equation:

$$R_{eff} = \frac{c_0 - c_e}{c_0} * 100$$

where R_{eff} is Removal efficiency (%), C_o is Initial Pb(II) concentration (mg/L) and C_e is Equilibrium Pb(II) concentration (mg/L)

- **Evaluation of Modified Adsorbents:** In order to improve the adsorption efficiency, a second experiment was designed to use chemically modified adsorbents. The adsorbents were prepared by:
    - Immersing the raw adsorbents in a potassium hydroxide (KOH) solution to alter their surface characteristics.
    - Drying of adsorbents at 110°C to lock the amendments.
    - Repeated adsorption efficacy testing under the same experimental conditions with unmodified adsorbents.

The modification process was calibrated to maximize functional group accessibility, porosity and Pb(II) ion retention efficacy. A number of studies conducted at 100, 150 and 200 °C temperature range revealed the role and influence of temperature on the efficacy of lead adsorption.

Adsorption capacity and efficiency were determined by calibrated equations determined from initial and the ultimate Pb(II) concentration. In addition, the chemically modified adsorbents were applied to enhance the heavy metal removal. These data are informative on the mechanics of adsorption and provide a road for further studies on adsorption kinetics and thermodynamics.

Results and Discussion

Lead removal from drinking water is still one of the most impactful environmental problems regarding toxicity and stability. Therefore, the present study has conducted a series of adsorption experiments to compare Pb removal performance under various conditions. Experimental parameters analysed were temperature (100°C, 150°C, 200°C), initial lead concentration (10–60 mg/L), contact time (30–180 min), pH (4–9) and adsorbent dosage (1–6 g). Effect of thermal activation on adsorption performance has been explored and role of pH on surface charge interactions and lead speciation was suggested. Contact time and adsorbent loading were, furthermore, studied in order to get understanding of the effect that these parameters have on adsorption kinetics and capacity. With the systematic optimization of these parameters, this work assures certain evidence on developing economic and efficient lead poison water treatment.

Effect of Temperature in Concentration Vs Adsorption Efficiency: The data sets reflect the effectiveness of lead adsorption from aqueous solutions with samples consisting of rubber seed shells, tamarind pod shells, groundnut shells and Pistachio shells for different initial lead concentrations (10–60 mg/L) at three different temperatures 100°C, 150°C and 200°C. The conclusions offer understanding of the effects of concentration and the temperature on adsorption efficiency. The adsorption efficiency is typically reduced as increasing the initial concentration of lead accumulates among all adsorbate and temperature conditions. This tendency indicates that with increasing concentration, the adsorption sites reach their maximum number, below which further adsorption is limited.

Nevertheless, at lower Pb(II) concentrations, the active adsorption site availability facilitates the higher Pb(II) removal capacity. Figure 1 depicts the concentration Vs adsorption efficiency graph with respect to various temperatures (100°C, 150°C and 200°C). Adsorption efficiency is minimum at 100°C applications in all tested adsorbents. Rubber seed shells demonstrated reduced adsorption performance e.g. decreased from 79.5% (rubber seed shells concentration of 10mg/L) to 72.92% (rubber seed shells concentration of 60mg/L).

Adsorption is significantly improved at 150°C. Rubber seed shells 84.5% and 82.8% yield at 10 mg/L and 60 mg/L respectively, indicating that temperature increase has a positive effect on adsorption. Efficiency is meanwhile still satisfactory at 200°C, but slightly declines, suggesting that thermal energy can be deleterious to adsorption. Rubber seed shells exhibited the greatest adsorption capacity under all conditions and thus is the most efficient adsorbent. Tamarind pod shells showed moderate but slightly lower performance compared to rubber seed shells while the groundnut shells showed the lowest performance across all shells for high lead concentration. Pistachio shell yielded the same efficiency as tamarind pod shell, however, showed decreased efficiency for high lead concentrations.

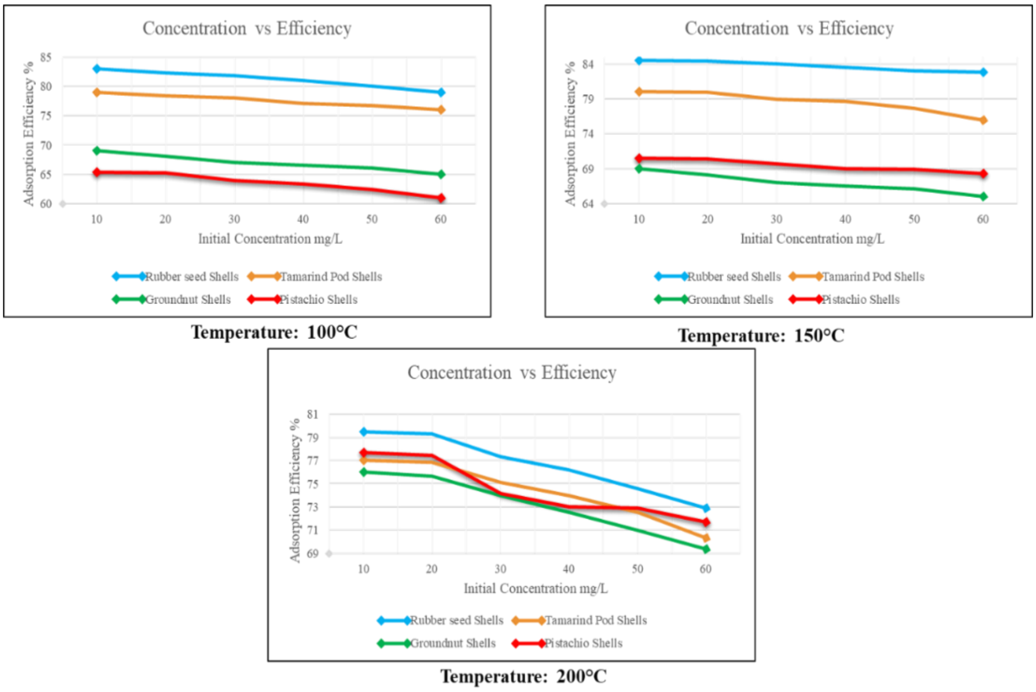

Figure 1: Concentration Vs Adsorption Efficiency graph with respect to various temperature (100°C, 150°C and 200°C)

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The optimal adsorption temperature was 150°C (the lower Pb+ concentrations led to better adsorption due to more active sites exposed). Rubber seed shells are demonstrated as a possible lead removal material in those conditions.

Effect of Temperature in Adsorbent Dosage Vs Adsorption Efficiency: The adsorption performance of several bio-based adsorbents such as rubber seed shells, tamarind pod shells, groundnut shell and Pistachio shells have been investigated in terms of the initial concentration of lead in an aqueous solution at 100°C, 150°C and 200°C. The observations from the datasets are discussed further. Adsorption efficiency decreases with increasing initial lead concentration at all temperatures. Under low concentration (10 - 30 mg/L), adsorption efficiency is highest and between high concentrations 40 - 60 mg/L, it decreases. The performance decrease with higher concentration is more significant for Pistachio shells and groundnut shells than rubber seed shells and tamarind pod shells.

Figure 2 shows the adsorption dosage Vs adsorption efficiency plot as a function of various temperatures. Adsorption efficiency is moderate at 100°C and reached 83% and 79% respectively for rubber seed shells and tamarind pod shells of 10 mg/L. Efficiency increases at 150°C, rubber seed shells yielding 84.5% showing increased adsorption kinetics. At 200°C, Pistachio shells increase from 65.4% to 77.7%, delivering that the higher temperatures favor stronger adsorbate-adsorbent interactions because of the increased molecular agitation and diffusion. Rubber seed shells are always the best adsorbate at any condition and tamarind pod shells are the next best adsorbate, with slightly compromised performance at higher concentrations.

Groundnut and Pistachio shells exhibit significant adsorption efficiencies, but diverge sharply at the higher dilutions. Adsorption is endothermic and heat strengthens the binding of lead ion to the adsorption site and also to that of the pores. However, excessive temperatures beyond 200°C may degrade adsorbents. Improvement of temperature as well as lead concentration can lead to an improved performance of bio-based adsorbents, namely rubber seed shells and tamarind pod shells in water decontaminating processes. The performance ranking is:

Rubber Seed Shells > Tamarind Pod Shells > Groundnut Shells > Pistachio Shells.

Effect of Temperature in pH Vs Adsorption Efficiency: The three data sets presented describe the performance of the various adsorbents (Rubber Seed Shells, Tamarind Pod Shells, Groundnut Shells and Pistachio Shells) at different adsorbent dosages in terms of adsorption performance. The data are all measurements of 100°C, 150°C and 200°C. The application of increasing adsorbent dosage result in higher adsorption efficiency in any temperature conditions. Rubber seed shells at 100°C have higher efficiency from 79.5% at 1 g to 82.9% at 6 g, while at 200°C, efficiency is from 71.43% at 1 g to 82.5% at 6 g. This trend is reproducible across all adsorbents, denoting that increased doses yield a larger number of active sites for lead ion adsorption. Adsorption is decreased at higher temperatures (200 °C), as compared to 100 °C and 150 °C and low adsorbent doses, which implies while modest temperature increases might elevate molecular interactions. Higher temperature levels could enhance desorption or weaker binding.

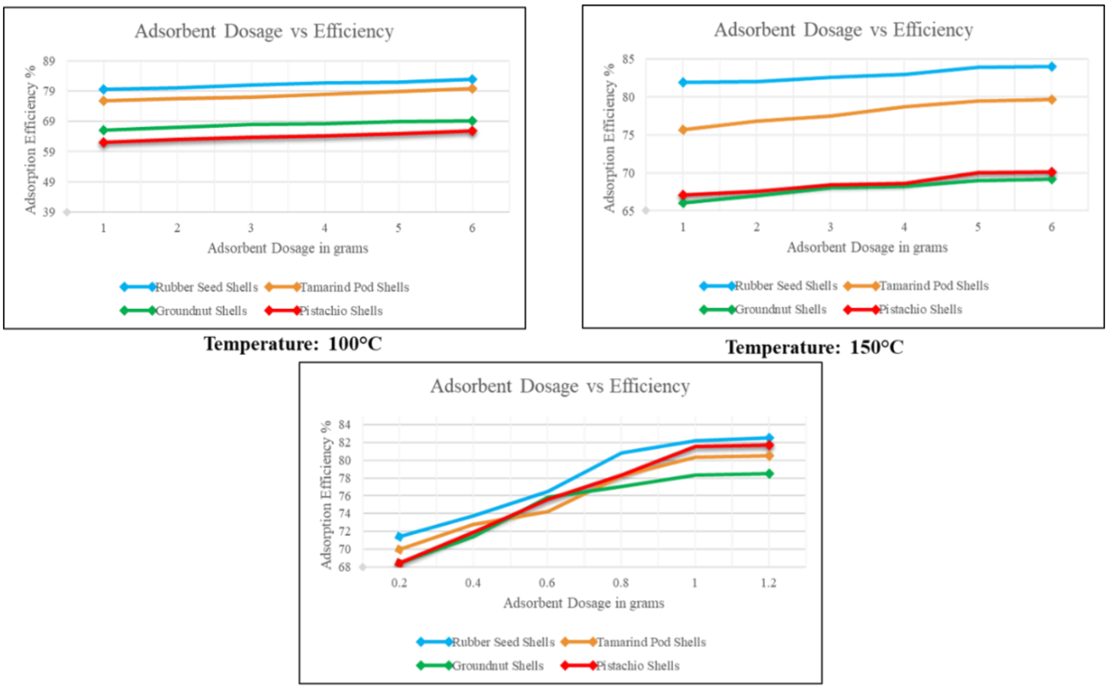


Figure 2: Adsorption dosage Vs Adsorption Efficiency graph with respect to various temperature (100°C, 150°C and 200°C)

When compared with all tested adsorbents, rubber seed shells showed the maximum adsorption capacity, suggesting a greater surface area with stronger chemical binding with lead ions. Groundnut and Pistachio shells exhibited lower adsorption but nevertheless the adsorption could be enhanced by increasing adsorbent amount. Nevertheless, as the concentration of adsorbent material further rises, the efficiency gain decreases because adsorption sites become saturated. Figure 3 depicts the pH Vs adsorption efficiency graph with respect to various temperatures (100°C, 150°C and 200°C).

Lead adsorptive efficiency is at the maximum for the rubber seed shells (RSS) as a function of pH 6-7 with yields of 83.7% at 100°C and 84.3% at 150°C. Efficiency decreases to 68.17% and 72% at pH 4 and 9 respectively, when it is utilized at 200°C due to adverse conditions. Competitive loss in the adsorption behaviour due to hydrogen ions in acidic environment and lead ion precipitation forming hydroxides in alkaline environments are limiting factors of the adsorption processes. Higher adsorbent dosages enhance effectiveness until the maximum is attained, beyond which no further benefits are accrued. Increased temperatures can trigger desorption, further reducing the adsorption efficiency. However, due to these factors, solid performance is consistently shown in RSS and it is a potential material for the removal of Pb from aqueous solution.

Effect of Temperature in Contact Time Vs Adsorption Efficiency: The results indicate that lead adsorption efficiency rises as the concentration of Pb ions increases at all temperatures (100°C, 150°C, 200°C) until reaching a saturation point when subsequent adsorption can proceed in a stable fashion or it slightly decreases. Higher temperature (200 °C) better accelerates adsorption due to stronger molecular kinetic energy that enables the adsorption of lead ion to the adsorbent surface more efficiently. Rubber seed shells are demonstrated to always perform better in adsorption at any temperature, indicating the good surface area as well as adsorption capacity. Tamarind pod shell and groundnut shells show moderate efficiency behavior and Pistachio shell shows the lowest efficiency, possibly due to the reduced number of active adsorption sites. The adsorption efficiency is also enhanced by prolonged contact time to equilibrium, after which further increase in contact time of the materials has no effect on their adsorption efficiency. At 200°C, adsorption occurs faster compared to lower temperatures. Rubber seed shells are fully exploited of contact time and contact temperature, demonstrating rapid adsorption kinetics. Contact time Vs adsorption efficiency diagram has been presented as a function of the different temperatures in figure 4.

Tamarind pod shells and groundnut shells have high adsorption properties, whereas Pistachio shells show low adsorption for the reason that there are not enough active sites. Rubber seed shells exhibit a high adsorption capacity for Pb removal which makes them the most efficient adsorbent. Adsorption performance typically increases with rising temperature by promoting the molecular interactions and diffusion. The process is endothermic and 100°C is an optimal working temperature for adsorption efficacy. Moreover, excessively high temperatures may trigger desorption. Adsorption increases in proportion to the increase in lead concentrations as long as there are enough active sites.

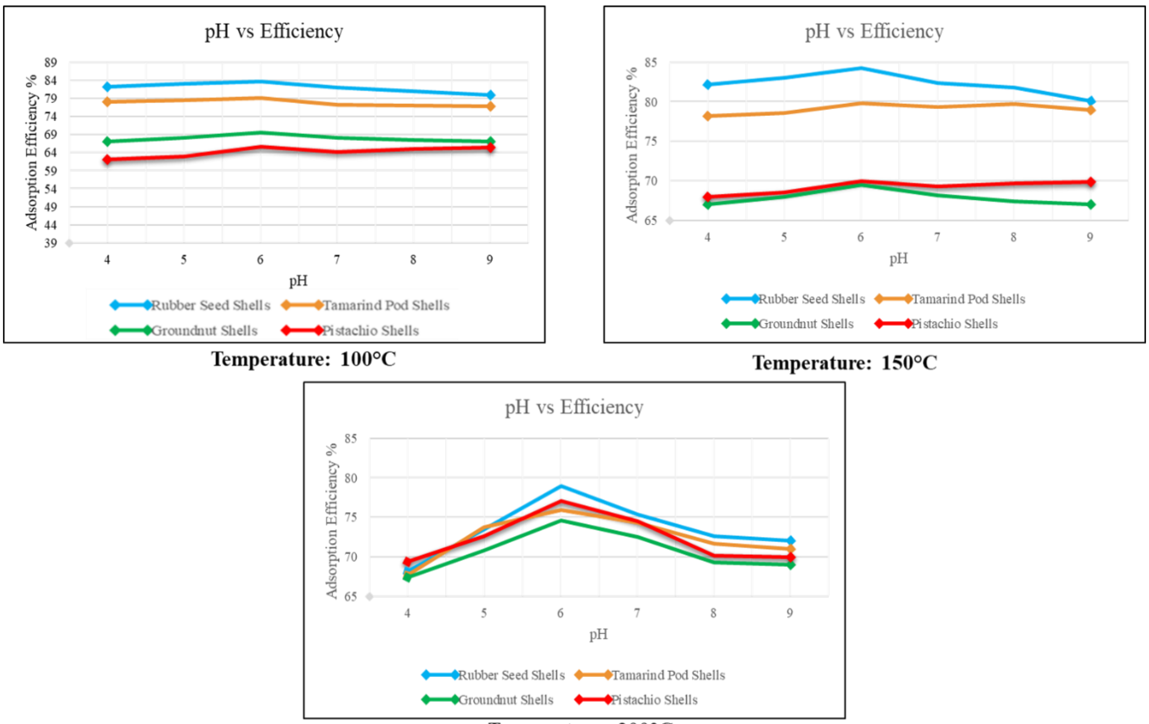
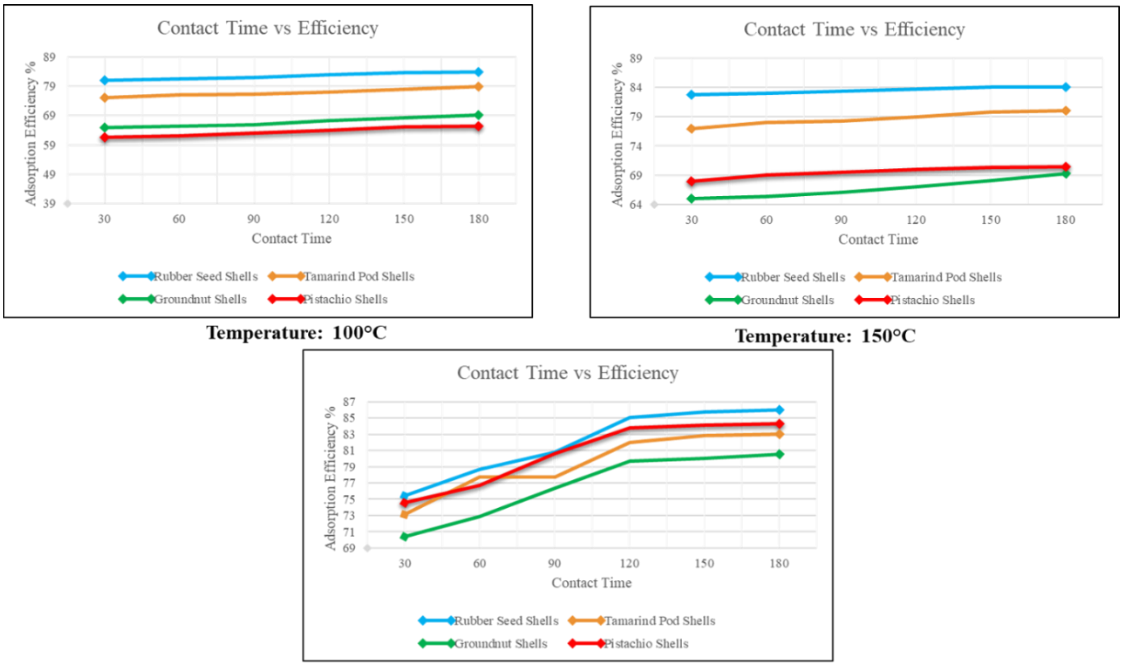


Figure 3: pH Vs Adsorption Efficiency graph with respect to various temperatures (100°C, 150°C and 200°C)



Temperature: 100°C

Temperature: 150°C

Temperature: 200°C

Figure 4: Contact time (min) Vs Adsorption Efficiency graph with respect to various temperatures (100°C, 150°C and 200°C)

Long-time contact enhances adsorption until equilibrium is reached. As a result, the study introduces the role of bio-derived adsorption materials for lead removal and the relevant combined effects of concentration, temperature and contact time on adsorption performance.

Adsorption Isotherm Modelling: Isotherm models of adsorption describe the amount adsorbed of an adsorbate onto adsorbent surface at equilibrium. These models are used to facilitate understanding of adsorption mechanism, adsorption capacity assessment and adsorption system optimization. The models Dubinin-Radushkevich (D-R), Redlich-Peterson and Sips are frequently used for the adsorptive (heterogeneous surface) characterization.

Dubinin-Radushkevich (D-R) Isotherm Model: The Dubinin-Radushkevich (D-R) model is a basic empirical equation that is mainly used to explain the adsorption of microporous materials. As opposed to Langmuir and Freundlich models, which implicitly assume preferential interactions, the D-R model takes adsorption in pores. The developed model with respect to the experimental data was plotted and is depicted in figure 5. The mathematical representation of the model would be given as follows:

$$q_e = q_m \, exp(-B\epsilon^2)$$

where q_e is equilibrium adsorption capacity (mg/g), q_m is maximum adsorption capacity (mg/g), B is activity coefficient related to adsorption energy (mol^2/J^2) and ϵ = Polanyi potential.

$$\epsilon = RT \, ln\left(1 + \frac{1}{C_e}\right)$$

The baseline setting employs a quadratic formula to relate the adsorbate equilibrium concentration, Ce, to the surface and internal temperatures of the adsorbent, X and I respectively in Kelvin units, as well as the universal gas constant (R 8.314 J/mol K) and absolute temperature T in Kelvins.

The model does not assume a homogeneous surface or monolayer adsorption. It is more appropriate for adsorption onto porous materials where the surface energy is non-uniform. The adsorption energy (B) can be used to determine the adsorption mechanism. When mean adsorption energy (E = $1/\sqrt{2B}$) below 8 kJ/mol is obtained, it indicates physisorption, while when mean adsorption energy (E) is above 16 kJ/mol, it indicates chemisorption.

Redlich-Peterson Isotherm Model: The Redlich-Peterson isotherm model is a hybrid adsorption model that combines the features of both Langmuir and Freundlich isotherms. It proposes an empirical parameter which enables to switch between Langmuir (at high concentration) and Freundlich (at low concentration) behavior and is thus more versatile for many adsorption systems. The developed Redlich-Peterson model was plotted with experimental data as depicted in figure 6. The mathematical representation of the model would be given as follows:

$$q_e = \frac{KC_e}{1 + aC_e^g}$$

where q_e = equilibrium adsorption capacity (mg/g), K is Redlich-Peterson constant (L/g), a is isotherm constant (L/mg) and g = dimensionless constant, approximately between 0 and 1.

When g=1, the model becomes the Langmuir isotherm, which gives monolayer adsorption. When g<1, it behaves as the Freundlich isotherm model, indicating surface heterogeneity. It offers a better approximation for experimental data, for which both of the Langmuir and Freundlich model cannot be applied separately.

Sips Isotherm Model: The Sips isotherm (or Langmuir-Freundlich isotherm) is another hybrid model to fit the adsorption on heterogeneous sites. It is of particular value when the adsorption sites exhibit different affinities to the adsorbate. The model behaves as the Freundlich isotherm at low concentrations and the Langmuir isotherm at high concentrations respectively and thus mitigates the drawbacks of both. The developed Sips model was plotted with experimental data depicted in figure 7.

Mathematically, the model would be presented as follows:

$$q_e = \frac{K_s {C^n}_e}{1 + a_s C_e^n}$$

where q_e is equilibrium adsorption capacity (mg/g), K_s is Sips equilibrium constant (L/g), a_s is Sips isotherm constant (L/mg) and n = heterogeneity factor (dimensionless).

If n = 1, the Sips model reduces to the Langmuir model which describes homogenous adsorption. When n<1, it is equivalent to the Freundlich model, representing surface heterogeneity. The model avoids unphysical infinite adsorption capacities for the high concentrations, as is typical of the Freundlich isotherm. Versatility tools are considered the Dubinin-Radushkevich (D-R), Redlich-Peterson and the Sips isotherm models for the characterization of the adsorption onto diverse surfaces. The D-R model is suitable for microporous materials and it is helpful to separate physisorption from chemisorption. The Redlich-Peterson equation is a hybrid, transferring between Langmuir and Freundlich behavior. The Sips model is especially suitable for adsorption on heterogeneous surfaces over a range of affinities.

Considering efficacy, the D-R model scores an R-squared value of 0.8643, the Redlich-Peterson model 0.9953 and the Sips model 0.9995. Because of its high performance, the Sips model was selected to be used in the feature engineering process of the machine learning model.

Table 1
Performance Metrics of Random Forest Regressor

Performance Metrics	Values
Root Mean Squared Error (RMSE)	0.00937
Mean Squared Error (MSE)	0.0009
R-Squared	0.97513

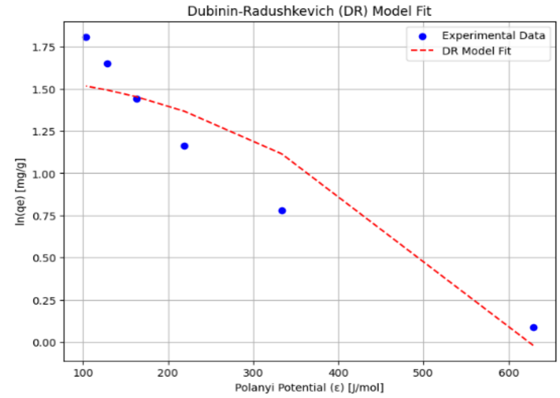


Figure 5: Dubinin - Radushkevich Adsorption Isotherm model

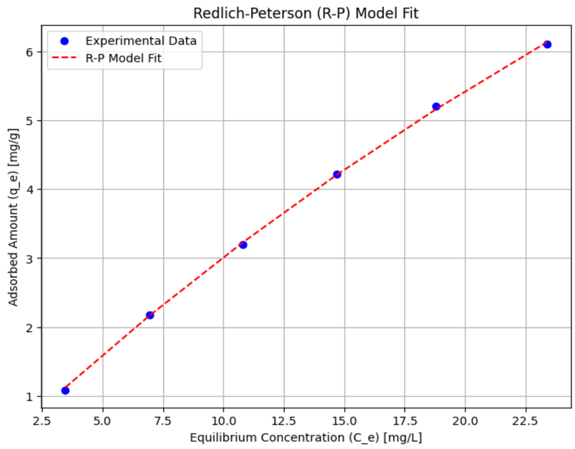


Figure 6: Redlich-Peterson Adsorption Isotherm model

https://doi.org/10.25303/301rjce045057

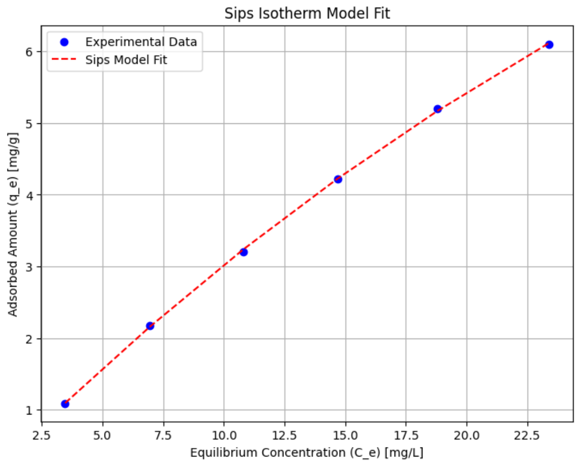


Figure 7: Sips Adsorption Isotherm Model

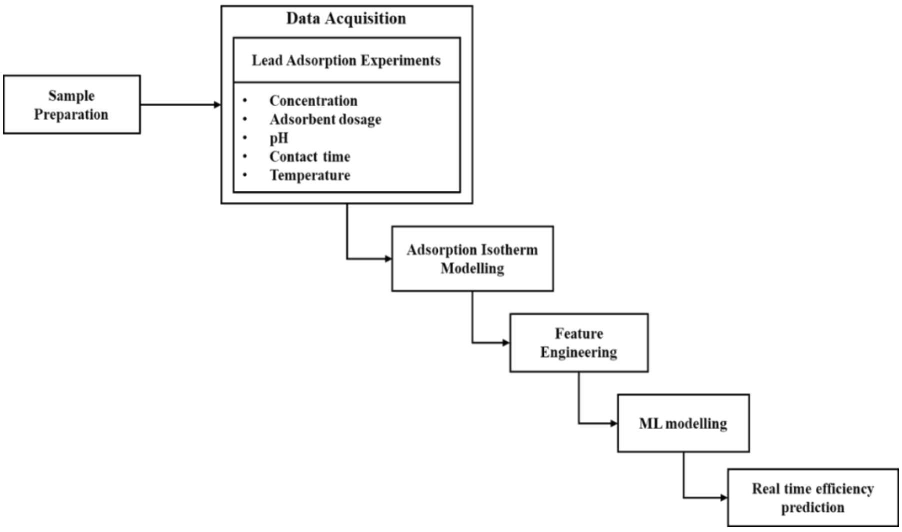


Figure 8: ML Prediction modelling

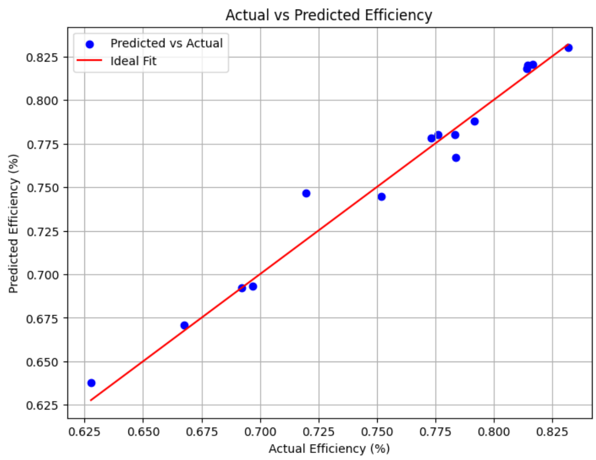


Figure 9: Random Forest regressor model

Machine learning modelling

Adsorption is one of the main capabilities used for wastewater treating, pollutant elimination and material separation. Accurate measurement of adsorption efficiency is of direct practical utility in the optimization of a process, yet, in a conventional experimental approach, much time can be wasted in the experiment. Computationally efficient data driven prediction would be provided by the ML models. Adsorption phenomena on surface heterogeneous systems have been accurately described in terms of the experimental data through the use of the Sips isotherm model (i.e. the hybrid Langmuir/Freundlich isotherm). They are connected to prediction models with the selected variables (initial adsorbate concentration, pH and contact time, adsorbent dose and temperature). Figure 8 showcases the ML prediction model development.

Such ML-based models are also valuable for reducing the huge experimental work, on-line, in real time, control and optimization of the adsorption process. The reason is that it is possible to delineate adsorption behaviour, as that is the key reason why it is feasible to go from the laboratory scale to the industrial scale, providing them in a reproducible way and in the case, to determine and make operating decisions based on them. The incorporation of real-time simulation prediction model into the system allows real-time monitoring and dynamic control of process parameters to obtain the optimal system performance for industrial or environmental use. Figure 9 depicts the model fit of Random forest regressor mode developed. Table 1 showcases the performance metrics of Random forest regressor model developed.

Future Scope

The research on adsorption-based water treatment is expanding to the combination of the advanced ML algorithms and the real-time monitoring devices for achieving the optimized performance of prediction. Accompanying studies on a broader set of sorbents i.e. nanomaterials, bio-adsorbents and composites have allowed a greater insight to be developed into the adsorption behaviour under changing environmental conditions. The IoT-based real-time monitoring systems will enable in-line process engineering and hence efficient adsorption in the treatment plants of industrial wastewater discharge streams.

Hybridized Deep learning models with LSTM and convolutional neural networks (CNNs) could be used to predict accuracy in realistic modeling of the intricate adsorption dynamics. In the end, the translatability of laboratory-based work-world environments to operational work-world environments will substantially rely on the validation of these models in operational environments.

Conclusion

This research work examines the adsorption efficiency of lead removal process from aqueous solutions across different temperature conditions using machine learning-based predictive modeling. According to experimental results, adsorption capacity tended to be dependent strongly on temperature. Generally speaking, higher temperature would promote adsorption and thus an endothermic adsorption mechanism is reasonable. Efficiency trends were explained by initial concentration, pH, contact time and adsorbent dose. The analysis has been performed by using a Random Forest Regressor model that has afforded an R^2 value (0.97513), the Root Mean Squared Error (RMSE) (0.00937) and the Mean Squared Error (MSE) (0.00009).

These results show how machine learning can be harnessed toward a reliable prediction of an adsorption efficiency using experimental variables. Isotherm model of Sips fitted well the non-linearity of adsorption kinetics using a concentration range and using deposition conditions, that permit the use of the model for adsorption modeling of various aqueous systems. Reported results demonstrate the potential of using machine learning to better implement the adsorption processes by offering the possibility to automate and optimize adsorption operation parameters in real time.

The use of machine learning models in adsorption studies is of great importance to the industry and the environment, such as industrial water treatment, real-time monitoring in adsorption-based purification, optimization of adsorbent utilization, automated smart systems etc.

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