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Removal of lead ions from aqueous solution using potassium hydroxide modified natural adsorbents

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As time progresses, a combination of human activities and natural occurrences releases contaminants, specifically heavy metals. These contaminants enter into water bodies, posing a threat to aquatic ecosystems and emphasizing the importance of implementing effective measures for pollution control and water quality preservation. This makes it necessary to treat water to reduce the negative impacts of toxic heavy metals in water and supply pure water for domestic and environmental use. Thus, the increased release of heavy metals like lead into the environment due to rapid industrialization has raised severe global concerns. This study aims to remove lead ions from water using a low-cost bio adsorbent. The present study examined the utilization of groundnut shells, tamarind pod shells, rubber seed shells, and pistachio shells as lead adsorbents. The adsorption efficiency is examined in relation to adsorbent dose, pH, contact time, and initial concentration, and the most efficient adsorption parameters are identified. In addition, adsorption mechanism, thermodynamics parameters and kinetic modeling are carried out to clarify the mechanism of adsorption. Isometric models, namely, Langmuir and Freundlich, are used to characterize the adsorption process, with better correlation to the Langmuir model. Kinetic observations indicated that adsorption in similar manner with transition of pseudo-second-order model and thermodynamic analysis confirmed the nature of spontaneous exothermic and spontaneous endothermic adsorption reaction. The pistachio shell emerged as the most effective of the four examined adsorbents, displaying the highest adsorption capacity of 88.9% at an adsorbent dosage of 1.2 g/L. This result underscores the superior performance of pistachio shells, positioning it as the optimal choice among the tested adsorbents.

Keywords: Adsorption isotherms, Adsorbent dosage, Contact time, Groundnut shell, Heavy metal, kinetic modeling, Pistachio shell, Rubber seed shell, Tamarind pod shell, Thermodynamics

Introduction

The most severe ecological crisis facing by humans today is environmental pollution, defined as the excessive release of undesired foreign substances into the environment, negatively altering the natural quality of the environment and endangering aquatic, plant, and animal life as well as human health[1]. It is commonly recognized that industrial wastewater contains a wide variety of organic and inorganic compounds[2]. Lead is a typical heavy metal that can be dangerous and is typically present in industrial wastes. It is an industrial contamination that seeps into the environment through the soil, water, and air. Due to its interference with numerous bodily functions, including the reproductive, kidney, heart, and central neurological systems, lead presents a significant health danger to humans if consumed or inhaled. The World Health Organization emphasizes the importance of having zero lead ion concentration by setting the maximum permissible lead concentration in drinking water at 0.01 mg/L[3].

Enough effluent treatment must be done to lower the amount of heavy metals in water before distributing clean water supplies to homes or the environment. Additionally, the discipline of environmental restoration was established with a number of traditional methods that can achieve the goal of removing heavy metal ions from the environment. Heavy metals can be removed using a variety of techniques, such as adsorption[4], chemical precipitation[5], evaporation, reverse osmosis[6], ion exchange, electrochemical extraction[7], and membrane processes.

Adsorption has been studied for a variety of water pollutants and shown to be one of the safest, most straightforward, and most economical techniques. Adsorption is often regarded as the most popular technology for removing heavy metals from systems due to its low cost, high efficiency, availability of a wide variety of adsorbents, ease of use, and relatively straightforward methodology. For the purpose of finding the best water treatment system, the

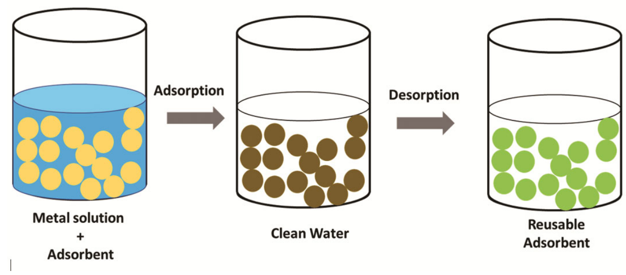

Fig. 1 — Mechanism of metal ion adsorption process

adsorption process meets the requirements to maximize heavy metal removal. Fig. 1 illustrates the mechanism of metal ion adsorption. The secret to any adsorption process is to choose the ideal component, known as an adsorbent. Bio-adsorbents made from plant wastes are thought to be an inexpensive and simple substitute for metal-containing water treatment systems.

In this study, we investigated the Pb(II) removal adsorption property of KOH treated natural adsorbents (groundnuts shells, tamarind pod shells, rubber seed shells and pistachio shells). The rubber seed shell (RSS) is mostly made up of ash, lignin, hemicellulose, and cellulose, whereas the kernel also contains organic substituents[8]. The components of a rubber seed kernel (RSK) are ash, protein, fat, and carbohydrates. There are no traces of inorganic substances in the lipids and cellulose that make up pistachio shells. Triglyceride and cellulose concentrations change with shell depth in accordance with the purpose of the shell at that particular depth. With a complex fibrous structure, the groundnut shell is a lignocellulosic substance made up of cellulose, hemicellulose, and lignin. The adsorption mechanism, thermodynamic parameters and kinetic process are systematically analyzed to understand the adsorption process well. Moreover, adsorption isotherm has been used to calculate the best-fit model for Pb(II) adsorption.

Experimental Section

Preparation of Materials

Careful measures were taken to guarantee the homogeneity and purity of the materials obtained in order to prepare the adsorbents for the lead removal studies. Rubber seed shells, tamarind pod shells, pistachio shells, and groundnut shells (shown in Fig. 2) were first collected and thoroughly cleaned with distilled water to remove any foreign matter. After being cleaned, the shells were kept for six hours in an oven for a regulated drying phase. After removing the dried samples from the oven, the shells were crushed and sieved to get a uniform particle size. Particles that were retained in a 150 µm sieve after passing through a 300 µm sieve were carefully gathered and kept for later testing. $Pb(NO_3)_2$ was dissolved in ultrapure water at different concentrations to create lead ion solutions.

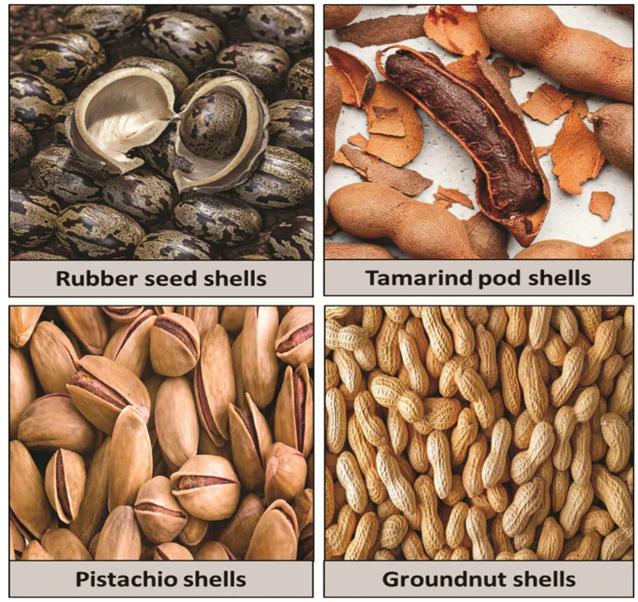

Fig. 2 — Picture of different seed shells used as adsorbents

To increase the effectiveness in removing lead, a methodical process was followed in its preparation. This procedure involved the individual immersion of 20 g of each adsorbent sample, which came from the shells of rubber seeds, tamarind pods, pistachios, and groundnuts, in a 200 mL solution of potassium hydroxide (KOH). During this phase, which lasted for 24 h at room temperature, the alkaline solution was able to adsorb and change the adsorbent materials. After immersing the samples for the designated amount of time, the samples were carefully filtered to remove any remaining liquid and contaminants from the KOH solution. The filtered samples were dried in the sun for 6 h and in an oven set to 80 °C for 6 h in order to finish the modification procedure.

Batch adsorption experiment

The intended mass of each adsorbent was combined with 50 mL of Pb(II) solution in batch tests carried out in 250 mL stoppered bottles. Using a water bath shaker with temperature control, the liquid was stirred at 298 K. Following the specified shaking period, the solid adsorbent was filtered out of the solution. By changing one parameter while holding the others constant, the parameters influencing adsorption efficiency were investigated. The trials were conducted with varying dosages, pH levels, contact time, and concentration.

The adsorption extent was determined using Eq. (1):

$$Q_e = \frac{c_o - c_e}{m} * v \quad \dots (1)$$

where c_o is the starting Pb(II) concentration, c_e is the Pb(II) concentration at equilibrium, m is the mass of adsorbent (g), and v is the volume of the Pb(II) solution in the bottle. Q_e is the metal adsorption capacity (mg/g). Using Eq. (2), the overall removal efficiency (R_{eff}) was determined.

$$R_{eff} = \frac{c_o - c_e}{c_o} * 100 \quad \dots (2)$$

A second set of tests was carried out to assess the modified adsorbents' efficacy in removing lead after they had been prepared by immersion in a potassium hydroxide solution and subsequent drying. In these tests, lead solutions were exposed to the modified adsorbents under carefully monitored circumstances.

Results and Discussion

The impact of these materials and additional variables on improving removal efficiency was assessed through testing at various concentrations (10, 20, 30, 40, 50, 60 mg/L) and with different contact times (30, 60, 90, 120, 150, 180 min). In addition, the effects of pH at levels of (4,5,6,7,8,9) and adsorbent dosage of (0.2, 0.4, 0.6, 0.8, 1.0, 1.2 g/L) were examined. The optimal lead removal effectiveness was attained using 1.2 g of pistachio shell, showcasing its exceptional adsorption capacity and reinforcing its potential as a highly efficient and eco-friendly remediation agent for lead-contaminated environments.

Effect of pH

The impact of varying pH on Pb^{2+} removal was assessed within the range of 4-9 for both modified and raw adsorbents. The elimination efficiency increased from pH 4 to 6, as in Fig. 3. Pistachio shells exhibited the utmost adsorption capacity at pH 6.0, emphasizing the significance of pH as a critical factor influencing the effectiveness of lead removal and highlighting the favourable adsorptive properties of pistachio shells within this specific pH range.

The adsorption activity was found to substantially decrease at pH values greater than 6.0, according to the observations. However, at pH levels lower than 5.0, a significant concentration of positive hydrogen ions may impede the adsorption process. As a result, the adsorption sites were positively charged, which had the effect of rejecting the Pb(II) cations. It is commonly known that beyond pH 6.0, lead ions begin to precipitate as $Pb(OH)_2$, which inhibits lead ion adsorption. Decrease in efficiency at pH 7, 8, and 9 as a result of lead ions precipitating as hydroxide ($Pb(OH)_2$).

Effect of Adsorbent Dose

For initial lead concentrations of 50 mg/L, the effect of adsorbent dosage on lead removal was investigated at an ambient temperature of 25 ± 2 °C and a contact time of 3 h. At an adsorbent dosage of 1.2 g/L, the greatest removal of lead was achieved, as shown in Fig. 4. A tendency that has been noted is that process efficiency increases with increasing dosage. Efficiency is observed to rise in proportion to the dosage of a pistachio shell, peaking at 88.9%.

Effect of Contact Time

With all other parameters held constant, the adsorption of lead at various contact time was investigated at an initial lead concentration of 50 mg/L. As contact time increases, adsorption increases and reaches its maximum (Fig. 5). Again, after 3 h of contact time, no more adsorption occurs. This could be because there was a strong solute concentration gradient at first, and no adsorbent sites were occupied.

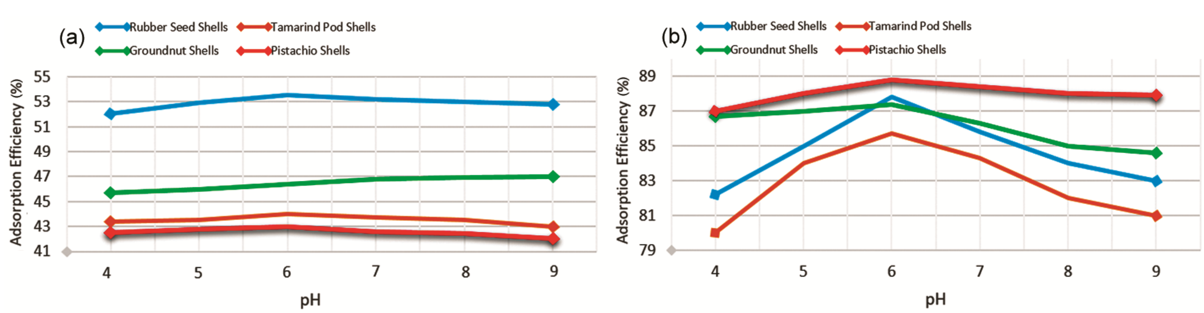

Fig. 3 — pH-Dependent adsorption efficiency of (a) raw and (b) modified adsorbents

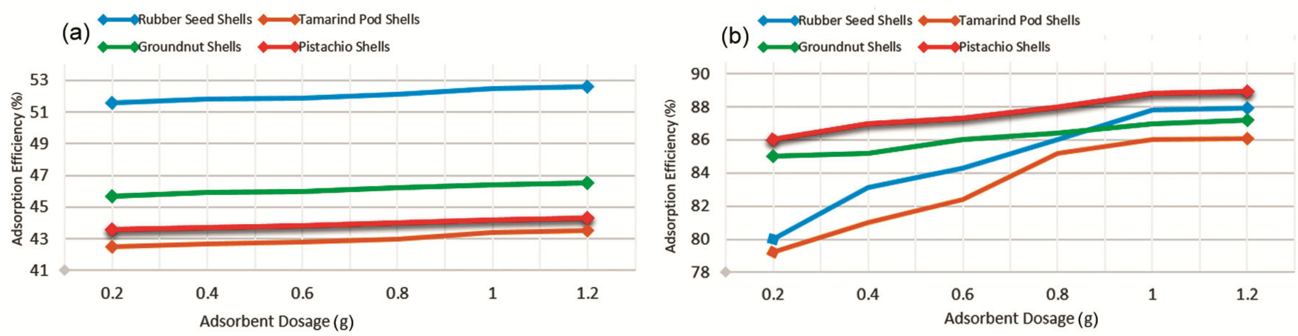

Fig. 4 — Adsorption dosage dependent adsorption efficiency of (a) raw and (b) modified adsorbents

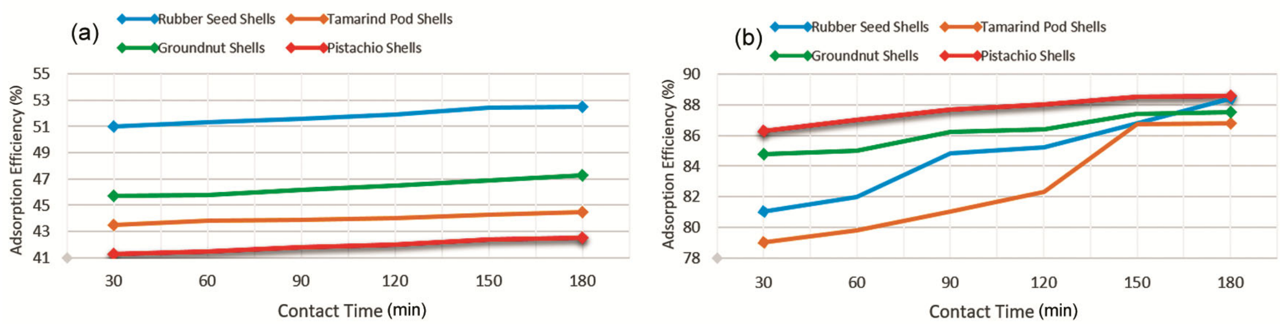

Fig. 5 — Contact time dependent adsorption efficiency of (a) raw and (b) modified adsorbents

Subsequently, the number of adsorption sites and lead concentration dropped, which resulted in a considerable decrease in the lead uptake rate by the adsorbent. A potential monolayer development of lead ions on the outer surface is indicated by a decrease in the clearance rate at the end of the trials. When adsorbents are examined for their adsorption efficiency, it becomes clear that pistachio shells work better than other materials. This indicates that pistachio shells are effective at adsorbing lead.

Effect of Concentration

Adsorption equilibrium of lead ions was performed with 20 mg of adsorbent at pH 5 and constant shaking time for a range of initial lead ion concentrations (5–25 mg/L for raw materials and 10–60 mg/L for modified materials). The adsorption capacity increases as the concentration of lead ions rises, as seen in Fig. 6. When comparing the adsorption efficiency of different adsorbents, rubber seed shells perform better when used as raw materials, and pistachio shells work better when used as modified materials. Based on the experimentations and the results obtained from them, the two performing adsorbents were selected to get utilized for adsorption isotherm model development.

Adsorption Isotherm Models

Models of adsorption isotherm characterize the equilibrium distribution of adsorbate molecules between the liquid phase and of the adsorbent surface at a fixed temperature. These models can aid not only in the description of the adsorption process, surface properties and adsorption capability of various materials. Langmuir, Freundlich, and Temkin isotherms are the most commonly isotherm models used.

Langmuir Isotherm Model

The Langmuir isotherm adopts monolayer adsorption on a flat surface, in which, all sites possess same energy and no interaction between adsorbed molecules is present. The model predicts that after a site has been colonized, no more adsorption occurs on that site and consequently adsorption saturation occurs with a maximum adsorption capacity. Fig 7 (a) and 7 (b) show the Langmuir models for Rubber seed shell and Pistachio pod shell, respectively.

The Langmuir equation is expressed as:

$$q_e = q_m . K_L . C_e / (1 + K_L . C_e) \qquad \ldots(1)$$

Where, q_e = Adsorbed amount per unit mass of adsorbent (mg/g), q_m = Maximum adsorption capacity (mg/g), K_L = Langmuir adsorption constant (L/mg)

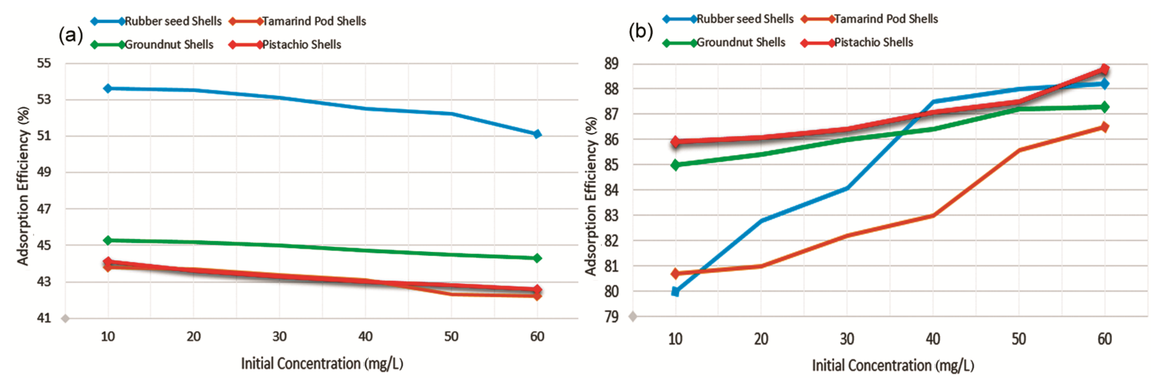

Fig. 6 — Initial concentration dependent adsorption efficiency of (a) raw and (b) modified adsorbents

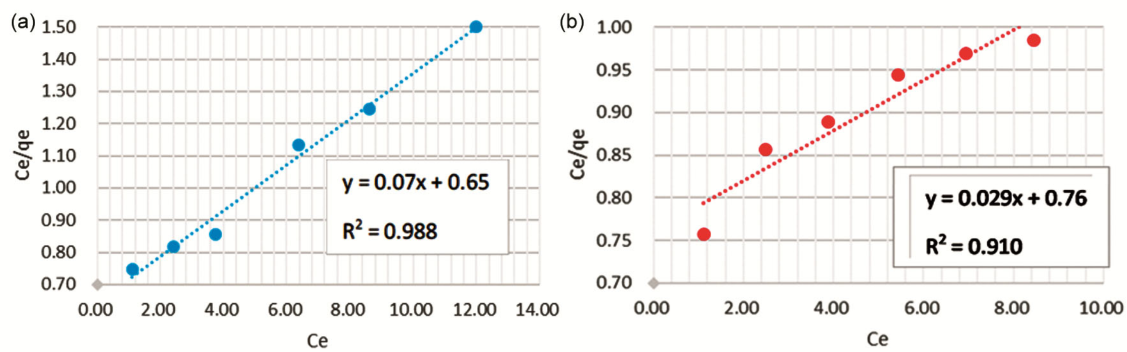

Fig. 7 — Langmuir model for (a) Rubber seed shell and (b) Pistachio pod shell

and C_e = Equilibrium concentration of adsorbate in solution (mg/L)

A key parameter resulting from this model is the separation factor (R_L), which defines the preference of adsorption:

$$R_L = 1 / (1+K_L .C_0) \quad \ldots(2)$$

where, C_0 is the initial adsorbate concentration. If $0<R_L<1$, adsorption is favorable and if $R_L>1$, adsorption is unfavorable.

Freundlich Isotherm Model

The Freundlich isotherm relates adsorption on a heterogeneous surface with non-uniform adsorption sites and uneven adsorption energy. In contrast to the Langmuir model, the Freundlich model accommodates multilayer adsorption, i.e., there is no limitation on the adsorption capacity.

The Freundlich equation is given as:

$$q_e = K_F C_e^{1/n} \quad \ldots(3)$$

Or in logarithmic form:

$$\log q_e = \log K_F + (1/n) . \log C_e \quad \ldots(4)$$

where, K_F = Freundlich constant representing adsorption capacity (mg/g), n = Adsorption intensity parameter (dimensionless) and C_e = Equilibrium concentration of adsorbate (mg/L)

The parameter 1/n indicates the adsorption favorability: If 0<1/n<1, adsorption is favourable, if 1/n=1, adsorption follows a linear process and if 1/n>1, adsorption is unfavorable. This model is widely used for describing physical adsorption (physisorption) and adsorption on natural materials such as activated carbon and bio-adsorbents. Figs 8 (a) and 8 (b) depicts the Freundlich models for Rubber seed shell and Pistachio pod shell, respectively.

Temkin Isotherm Model

The Temkin isotherm considers adsorbate-adsorbent interaction and postulates that adsorption energy decreases with surface coverage, because of adsorbate-adsorbate steric repulsion. This model, in addition, assumes that the adsorption heat decreases linearly, as opposed to a logarithmic decrease as in the Freundlich model. Figs 9 (a) and 9 (b) depicts the Temkin model for Rubber seed shell and Pistachio pod shell, respectively.

The Temkin equation is given as:

$$q_e = (RT/b) . \ln (K_T . C_e) \quad \ldots(5)$$

or in simplified linear form:

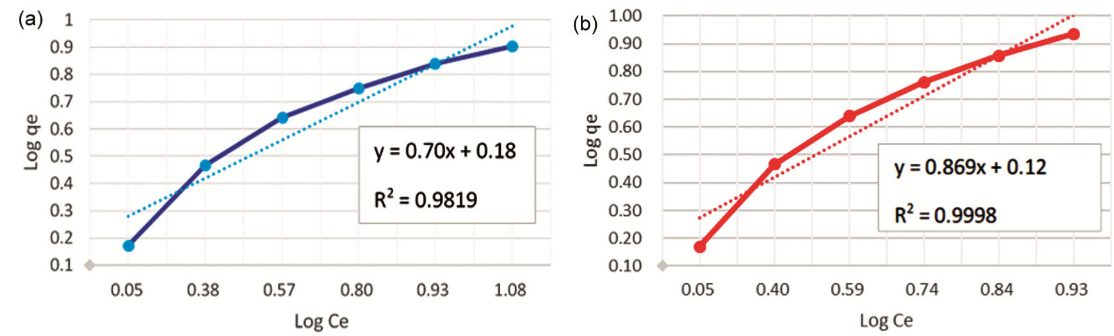

Fig. 8 — Freundlich model for (a) Rubber seed shell and (b) Pistachio pod shell

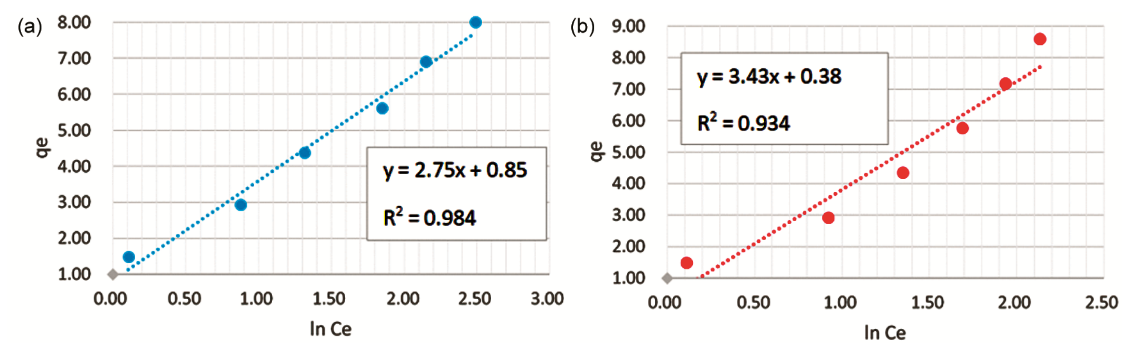

Fig. 9 — Temkin model for (a) Rubber seed shell and (b) Pistachio pod shell

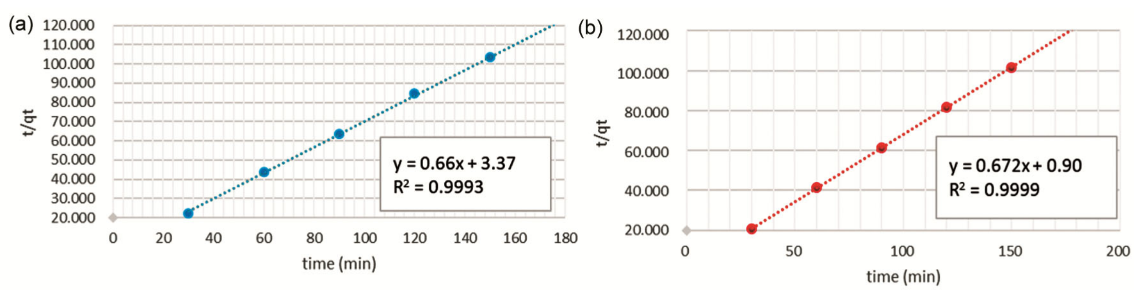

Fig. 10 — Pseudo-second order model for (a) Rubber seed shell and (b) Pistachio pod shell

$$q_e = B \ln K_T + B \ln C_e \qquad \ldots(7)$$

where, q_e = Adsorbed amount per unit mass of adsorbent (mg/g), K_T = Temkin isotherm equilibrium binding constant (L/g), B = Constant related to adsorption heat (B=RT/B), R = Universal gas constant (8.314 J/mol K), T = Temperature (K), b = Temkin adsorption energy constant (J/mol) and C_e = Equilibrium concentration of adsorbate (mg/L)

The Temkin model yields information on the adsorption energy distribution and is suitable when adsorbate-adsorbent interactions are important. It is of special use for modeling adsorption in liquid-phase adsorption systems with surface heterogeneity and non-covalent interactions of medium strength.

The choice of the proper fit isotherm model depends, among many other factors, on the experimental data and type of adsorption. Langmuir model, also suitable, for this type of systems, if adsorption occurs at well-defined sites only, Freundlich model is suitable for heterogeneous surfaces, and if adsorption interaction energy decreases with the adsorption-adsorbent interaction, the Temkin model is suitable.

Freundlich model (R^2 0.99), as depicted in Figs 10 (a) and 10 (b) for rubber seed and pistachio pod shells, respectivley, fit significantly better than the Langmuir model (R^2 0.92), as demonstrating the monolayer adsorption with monolayer adsorption capacity of 52.63 mg/g of pistachio shell. Kinetics of adsorption was described by pseudo-second-order model (R^2 0.99), and chemisorption mechanism is assumed to be the major interaction process. The thermodynamic parameters are discussed below.

- ΔG indicated negative values, therefore consistent with the spontaneous adsorption of Pb(II).
- ΔH was positive (27.3 kJ/mol), which indicates an endothermicity of the process.
- ΔS was positive, i.e., greater randomness at the solid-liquid interface during adsorption.

Among the investigated adsorbents, pistachio shells possessed the greatest adsorption capacity. Adsorption was kinetically and isothermally optimized using Freundlich isotherm and pseudo-second-order kinetic model, respectively, which evidenced monolayer adsorption and chemisorption as the main adsorption mechanism. Thermodynamic analysis further denotes the spontaneity and endothermicity of the process. These findings show the highly advantageous use of pistachio shells as an inexpensive way to remove heavy metals in wastewater treatment.

Conclusion

Removal of Pb(II) ions using four distinct naturally occurring adsorbents, namely groundnut shell, tamarind pod shell, rubber seed shells, and pistachio shell were studied. According to experimental studies, the ideal parameters for the effective removal of Pb(II) ion using rubber seed shells were 0.60 g, 180 min of contact time, pH of 6, and adsorbent dosage of 1.2. Through comprehensive analysis of various parameters, it is evident that while the rubber seed shell demonstrates a notable efficiency of 88.4% at a contact time of 180 s, exhibits superior performance across multiple factors. With its highest efficiencies recorded at optimal pH values, adsorbent dosages, and lead concentrations, reaching 88.8% and 88.9%, 88.8%, respectively, the rubber seed shell emerges as the most effective adsorbent overall, showcasing its versatility and efficacy in lead removal processes. Rubber seed shell exhibited the highest adsorption capacity as compared to the other promising adsorbates. The adsorption behavior fitted well to the Langmuir isotherm model and pseudo-second-order kinetic model, which showed monolayer adsorption and chemisorption as the main process. As determined by thermodynamic analysis, it was endergonic and thus spontaneous reaction. These results demonstrate the possibility of rubber seed shells served as a green, inexpensive, green, and environmentally friendly sustainable adsorbent for wastewater heavy metal removal. Collectively, these advantageous qualities position the adsorbent as a favourable choice not only for lead removal but also as a promising solution for addressing the presence of additional harmful metal ions in water systems.

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