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REMOVAL OF HEAVY METALS FROM INDUSTRIAL WASTEWATER USING EGG-SHELL ACTIVATED CARBON

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ABSTRACT
This study explores the preparation and application of eggshell activated carbon (ESAC) as an efficient adsorbent for the removal of heavy metals, specifically lead (Pb) and nickel (Ni), from industrial wastewater. The study involved characterization of ESAC to determine its physical and chemical properties, followed by adsorption experiments to assess its efficiency in heavy metal removal. ESAC was synthesized from waste eggshells and thoroughly characterized using BET surface area analysis, SEM, XRD, and FTIR to confirm its adsorption properties. Experimental adsorption tests showed that ESAC achieved removal efficiencies of 80% for lead and 65% for nickel under optimized conditions including pH, adsorbent dosage, contact time, and initial metal concentration. Adsorption isotherm analysis revealed that the Freundlich model best described the adsorption process, with Freundlich constants KF of 0.25 mg/g for Pb and 0.21 mg/g for Ni, indicating favourable adsorption. The Langmuir maximum adsorption capacities (qmax) were 45.7 mg/g for Pb and 41.2 mg/g for Ni. A comparative cost-benefit analysis highlighted the economic advantages of using ESAC over conventional activated carbon, that is, ESAC production costs were significantly lower compared to commercial activated carbon, highlighting its economic viability. This study confirms the potential of eggshell-derived activated carbon as an eco-friendly and economical solution.

Keywords: eggshell activated carbon, heavy metal removal, lead, nickel, adsorption isotherm, wastewater treatment.

1. Introduction

The expansion of industrial activities, urban development, and extensive chemical application in farming practices has resulted in the widespread discharge of both organic and inorganic contaminants, especially heavy metal pollutants, into environmental matrices. Aquatic contamination originating from manufacturing facilities presents particular concern owing to the persistent characteristics, harmful properties, and tendency toward biological accumulation exhibited by heavy metals including Pb, Hg, Cu, Ni, Cd, and As [1-4]. These toxic elements, present even in minute concentrations, create substantial hazards for ecological systems and human well-being, given their non-degradable nature and capacity to undergo biomagnification throughout trophic levels.

Table 1: The impact of the heavy metals on human body and the permitted amounts

Common heavy metal	Main sources	Main organ and system affected	Permissible Limits
Lead (Pb)	Lead-based batteries, solder, alloys, cable sheathing pigments, rust inhibitors, ammunition, glazes, and plastic stabilizers.	Bones, liver, kidneys, brain, lungs, spleen, immunological system, haematological system, cardiovascular system, and reproductive system.	***10***
Cadmium (Cd)	Batteries, paints, steel industry, plastic industries, metal refineries, and corroded galvanized pipes.	Bones, liver, kidneys, lungs, testes, brain, immunological system, and cardiovascular system.	***3***
Nickel (Ni)	Stainless steel and nickel alloy production.	Lung, kidney, gastrointestinal distress, pulmonary fibrosis, and skin.	***70***
Mercury (Hg)	Thermometers, fluorescent lamps, dental amalgams, gold mining, and coal combustion.	Brain, kidneys, liver, nervous system, and immune system.	***2***
Arsenic (As)	Pesticides, wood preservatives, smelting process and contaminated water	Kidney, liver, respiratory tract and skin	***10***
Zinc (Zn)	Galvanized metal, brass production, dietary supplement and fertilizers	Liver, Kidney, blood, nervous system and immune system	***300***

Table 2: Heavy metals present in effluent discharged by different industries

Industry	Heavy metals present in the efficient
Chloro-alkali	Cr, Cd, Cu, Pb, Zn, Hg, Se
Paints and dyes	Cr, Cd, Cu, Pb, Zn, Se
Petroleum refinery	Cr, Cd, Cu, Pb, Zn
Fertilizers	Cr, Cd, Cu, Pb, Zn, Hg, Mn, As
Motor vehicles	Cr, Cd, Pb, Zn, Hg, Se
Mining and metallurgy	Cr, Cd, Cu, Zn, Hg, Se, As, Ni
Stainless steel and nickel alloy production	Fe, Ni

Addressing contaminated wastewater has prompted researchers to develop new treatment approaches that are both economically viable and environmentally sustainable. Multiple techniques are available for extracting heavy metals, including precipitation methods, exchange processes, oxidation-reduction reactions, membrane technologies like reverse osmosis and ultrafiltration, electrodialysis, and adsorptive treatments [5,6]. Among these, adsorption stands out as the most efficient due to fewer drawbacks like sludge production, low efficiency, and high costs seen in other techniques. It offers design flexibility, produces high-quality effluent, allows adsorbent regeneration, and effectively removes diverse pollutants. This study chose adsorption for its proven efficiency across different conditions and broad contaminant removal capability [7]. ESAC has demonstrated considerable promise as an adsorptive material for eliminating heavy metal contaminants from aqueous systems. Eggshells, primarily composed of calcium carbonate ($CaCO_3$), are an abundant biowaste that can be converted into a highly porous and functional material suitable for adsorption applications [8-10]. The activation process enhances the surface area and introduces functional groups, making ESAC effective in capturing heavy metal ions through both physical and chemical adsorption mechanisms. Analysis through multiple analytical methods—including BET surface area measurements, SEM imaging, FTIR spectroscopy, and XRD analysis—validates that ESAC possesses the physical structure and chemical characteristics necessary for effective environmental cleanup applications, particularly in removing contaminants.
This study specifically addresses the severe heavy metal pollution in the Vrishabhavathi River, Karnataka, India, where industrial effluents have led to concentrations of Pb and Ni far exceeding permissible limits.

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Figure 1: Hydropower site (Virshabhavati River)

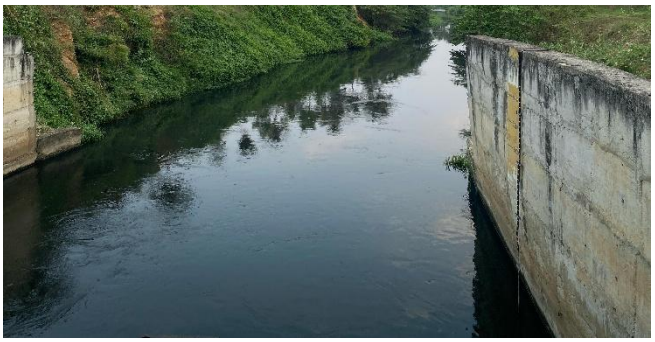

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Figure 2: Bidadi and Harohalli Industrial area

research validates ESAC's potential for these metal species by assessing its performance across multiple process variables including solution pH, adsorbent amount, and reaction duration [11]. The use of ESAC not only offers a sustainable approach by valorizing waste eggshells but also provides a cost-effective alternative to commercial activated carbons, making it particularly relevant for regions facing economic and environmental constraints [12,13]. Despite challenges such as reliance on external laboratories for advanced material characterization, financial limitations, and logistical hurdles in sample collection, the study successfully demonstrates the potential of ESAC in industrial wastewater treatment. These discoveries validate the use of eggshell-based activated carbon as a sustainable, low-cost, and proficient adsorbent for removing heavy metals, contributing to enhanced water purity, protection of community health, and eco-friendly waste recycling approaches.

A conceptual framework provides a visual representation of how different variables interact within a study (Perfetti, 2012). This investigation examines ESAC's effectiveness in extracting lead and nickel from industrial effluents as the outcome variable. The factors influencing this outcome include ESAC's physical and chemical characteristics, the process conditions that affect removal performance, and the economic feasibility through cost-benefit analysis.

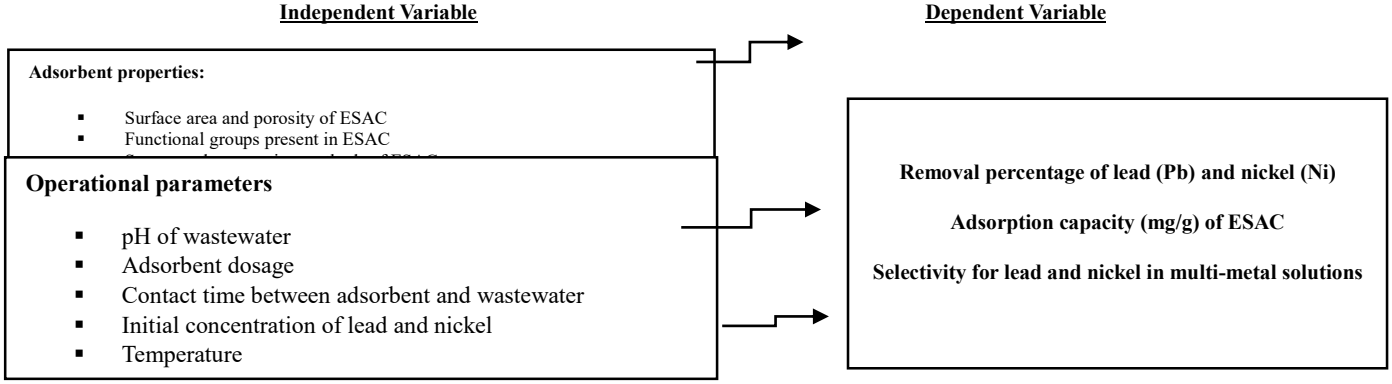

Figure 3: Conceptual framework

Eggshell activated carbon (ESAC) is produced by chemically and thermally treating waste eggshells, resulting in some porous material rich in functional groups that facilitate metal ion adsorption [14,15]. Numerous studies have demonstrated ESAC's high adsorption capacities for Pb, Ni, and other heavy metals, often comparable or superior to commercial activated carbons. Characterization methods like BET surface area analysis, SEM, FTIR, and XRD confirm the structural and chemical properties that contribute to ESAC's effectiveness. Additionally, modifications such as magnetic composites or blending with other materials have further enhanced adsorption performance and reusability [16-20]. Comparative research highlights that ESAC not only offers high removal efficiencies but also presents a sustainable and low-cost alternative to commercial adsorbents. Researchers have found that adsorption works best when certain factors—including pH, how long materials are in contact, and the amount of adsorbent used—are optimized. The adsorption behavior usually aligns with standard models (Langmuir or Freundlich isotherms) and follows pseudo-second-order kinetic patterns. Despite promising laboratory results, there is a need for systematic evaluation of ESAC's performance against commercial activated carbons under identical industrial wastewater conditions to establish its practical applicability and cost benefits [21-23].

ESAC emerges as an attractive option for treating heavy metal-laden industrial wastewater, offering the dual benefits of waste material transformation and pollution control. Moving forward, research efforts should prioritize investigating the material's durability over extended use, capacity for regeneration and reuse, and potential for industrial-scale deployment. Filling these research voids through systematic comparisons will enable the creation of economically sound and environmentally responsible treatment technologies. The present work aims to quantify ESAC's effectiveness in removing lead and nickel contaminants by analyzing adsorption behavior across multiple experimental conditions—pH levels, adsorbent dosing, reaction time, and pollutant concentrations—while benchmarking the removal performance for each metal species.

2. MATERIALS AND METHODS

This work investigates the potential of activated carbon prepared from eggshells as an affordable, eco-friendly solution for treating Pb and Ni contamination in Vrishabhavathi River industrial wastewater. Material characterization through BET analysis, XRD, SEM, and FTIR will reveal its surface and structural attributes relevant to adsorption. Batch experiments will systematically evaluate removal efficiency by varying operational parameters: adsorbent amount, treatment duration, pH conditions, and initial contaminant concentrations. Trace metal concentrations will be quantified using Atomic Absorption Spectroscopy (AAS), alongside

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measurements of pH, TDS, temperature, DO, and electrical conductivity to fully profile the wastewater. This approach leverages eggshell waste's high calcium carbonate content and porous structure to provide an effective, eco-friendly solution for heavy metal remediation.

2.1.1 Chemical Activating Agent: Sodium Hydroxide (NaOH) Sodium hydroxide (NaOH) was employed as the chemical activating agent to modify eggshell powder. NaOH facilitates the breakdown of organic components and promotes the development of porous structures during thermal treatment [24]. The chemical reaction between sodium hydroxide and $CaCO_3$, the predominant eggshell component, generates calcium hydroxide and sodium carbonate, leading to enhanced physical and chemical attributes of the activated carbon.

2.1.2 Raw Material (i): Eggshells: Waste eggshells (~700 g) were collected from local cafes and restaurants, washed with distilled water, sun-dried for 24 hours, and ground into fine powder (particle size ~150 µm). The powder underwent chemical activation by impregnation with NaOH solutions of varying molarity (0.5–1.5 M), stirred for 3–6 hours, and left for 24 hours at room temperature to ensure thorough absorption [25]. Post-activation, samples were washed to remove excess NaOH, dried at 80°C, and carbonized at 600°C to develop porous activated carbon [26]. The eggshell-derived activated carbon exhibits enhanced surface area and porosity, critical for effective adsorption.

2.1.3 Raw Material (ii): Industrial Wastewater Samples . Industrial wastewater samples were collected from five stations (S1–S5) along the Vrishabhavathi River, Karnataka, India, covering upstream (reference), midstream (industrial discharge), and downstream (agricultural impact) zones over three months (January–March 2025). Grab sampling was conducted using pre-cleaned, acid-washed polyethylene bottles to avoid contamination. Water quality indicators such as pH, turbidity, electrical conductivity, alkalinity, TDS, and DO were determined through electrometric measurement techniques and titrimetric procedures. The levels of heavy metals (Pb and Ni) were analyzed using Atomic Absorption Spectroscopy (AAS), a highly sensitive and specific analytical method with detection capabilities at parts-per-billion concentrations, guaranteeing accurate quantification of contaminant concentrations present in the effluent samples. The physicochemical analysis of industrial wastewater samples collected from five stations (S1–S5) along the Vrishabhavathi River between January and March 2025 revealed significant variations in water quality parameters [27-29].

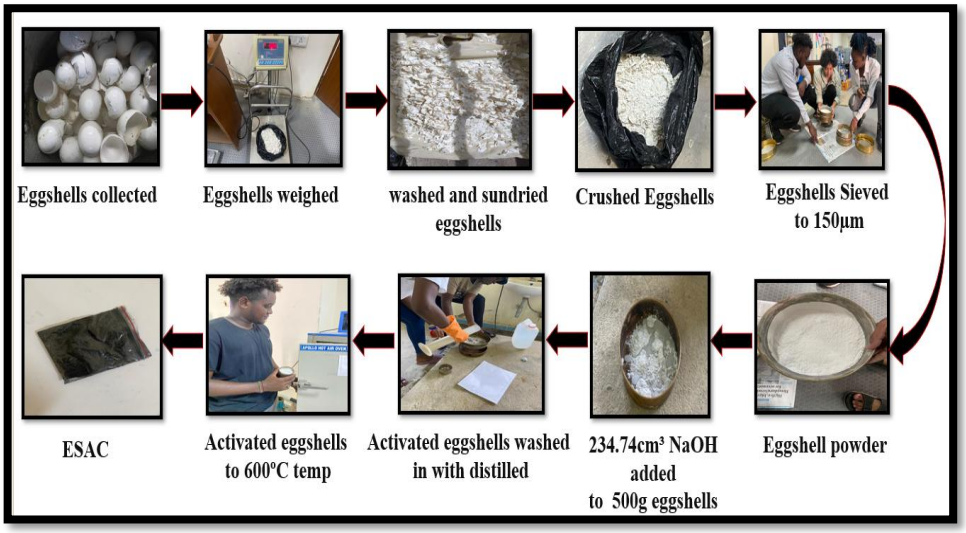

Figure 2.1 ESAC Preparation process

Figure 2.2 Sample collection points along Vrishabhavati River.

Turbidity values ranged from 105 to 291 NTU, substantially exceeding the permissible limit of 10 NTU, indicating high levels of suspended solids and pollution. The pH remained relatively stable, varying between 6.6 and 8.2, within acceptable regulatory limits, suggesting near-neutral to slightly alkaline conditions. Electrical conductivity (0.477–1.503 mS/cm) and total dissolved solids (342–987 mg/L) fluctuated moderately but stayed well below the permissible thresholds, reflecting consistent ionic content and dissolved mineral levels. Alkalinity ranged from 91 to 195 mg/L as $CaCO_3$, indicating moderate buffering capacity without significant pollution impact.

Dissolved oxygen (DO) levels showed considerable variability, ranging from 2.7 to 6.2 mg/L, with some stations experiencing lower DO concentrations that may indicate localized oxygen depletion and potential stress on aquatic organisms. Overall, while parameters such as pH, EC, alkalinity, and TDS generally complied with regulatory standards, elevated turbidity and episodic DO depletion highlight ongoing pollution challenges in the river. The data demonstrate an urgent need for competent wastewater treatment methods to mitigate contamination and safeguard the ecological balance of the Vrishabhavathi River.

2.1.4 Atomic absorption spectrophotometry (AAS)

Atomic absorption spectrophotometry serves as a precise analytical tool commonly employed for identifying and measuring minute quantities of heavy metals in industrial effluents. This technique operates by quantifying how much light at characteristic wavelengths—usually between 190 and 900 nm in the UV-visible spectrum—is absorbed by gaseous atomic species produced when samples are atomized in a flame [30]. Since different metals absorb radiation at distinct wavelengths, and absorption intensity correlates directly with elemental concentration, AAS enables accurate metal quantification. The analytical process involves several key steps: preparing the sample in solution form, creating blank and standard solutions, and calibrating the instrument using these standards. A calibration curve is plotted by measuring the absorbance of known concentrations, which is then used to determine the concentration of metals in unknown samples. The instrumentation typically includes a flame burner for atomization, a hollow cathode lamp as a light source, a monochromator, and a detector.

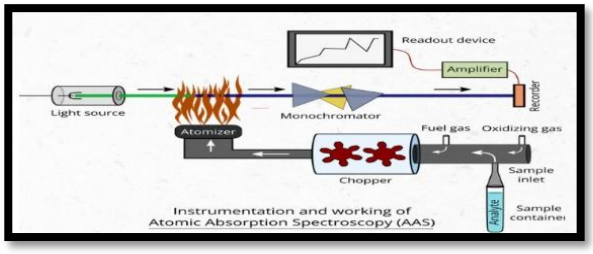

Figure 2.3 Instrumentation and working of AAS

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In environmental and industrial monitoring contexts, AAS is highly regarded due to its remarkable sensitivity (identifying metals at ppb levels), analytical specificity, cost-efficiency, and straightforward methodology. It is especially effective for analyzing metals like copper, lead, zinc, and cadmium in wastewater, making it a preferred technique for regulatory compliance and pollution assessment in industrial settings [31].

2.2 Methods

2.2.1 **Characterization of ESAC:** Evaluating eggshell-derived activated carbon requires thorough analysis of its physical structure, surface characteristics, chemical composition, and morphological features to verify effective activation and assess its adsorptive performance. This evaluation typically employs several analytical techniques: SEM for visualizing surface texture and porous architecture, XRD for analyzing crystal structure and material phases, FTIR for detecting functional groups present on the surface, and BET analysis for quantifying specific surface area and porosity. Together, these analytical approaches reveal essential information about ESAC's material quality, surface reactivity, and capacity for contaminant uptake [32,33].

a. **Scanning Electron Microscopy (SEM)** Scanning Electron Microscopy (SEM) analysis is crucial in the characterization of eggshell-derived activated carbon as it provides detailed insights into the surface morphology and porosity of the material. SEM images reveal the rough and irregular surface texture formed during the activation process, which creates cracks, fissures, and interconnected pores essential for adsorption applications. These pores significantly enhance the surface area, making eggshell activated carbon highly effective for adsorbing heavy metals like lead and nickel from wastewater [35]. Additionally, SEM analysis helps identify structural features such as pore distribution and size, which are critical for understanding adsorption mechanisms and optimizing material performance. For instance, eggshell activated carbon prepared using chemical activation methods has been shown to exhibit superior porosity compared to other adsorbents like groundnut shells, among others.

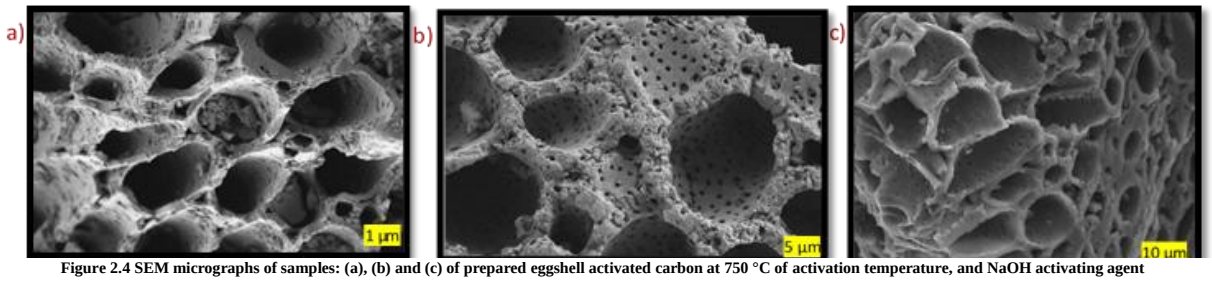


Figure 2.4 SEM micrographs of samples: (a), (b) and (c) of prepared eggshell activated carbon at 750 °C of activation temperature, and NaOH activating agent

Figures (a), (b), and (c) present microscopic views of eggshell-derived activated carbon at multiple magnifications. The substantial BET surface area results from the material's highly developed porosity. During carbonization, NaOH activating agent volatilization creates these pores by leaving behind spaces it once occupied. The calcination step promotes surface area enhancement. Among critical factors influencing activated carbon properties, temperature—or thermal effect—plays a paramount role. Surface active site generation through this thermal process enables adsorption functionality, producing the microporous and mesoporous architecture typical of activated carbon.

b. **X-ray Diffraction (XRD)**

The XRD technique offers powerful capabilities for assessing the structural crystallinity and phase makeup of activated carbon produced from eggshells. The XRD spectrum reveals key structural features, such as crystallinity, microstrain, and average crystallite size. In ESAC, sharp diffraction peaks—particularly at 2θ values of approximately 26° and 43°, corresponding to the (002) and (100) planes—indicate the presence of partially ordered graphitic carbon [36]. These peaks, defined by Miller indices, confirm successful carbonization and the formation of graphitic layers with a disordered structure. The broadness of these peaks, especially at higher angles, suggests the coexistence of amorphous carbon phases, which are typical in activated carbons due to their highly porous nature.

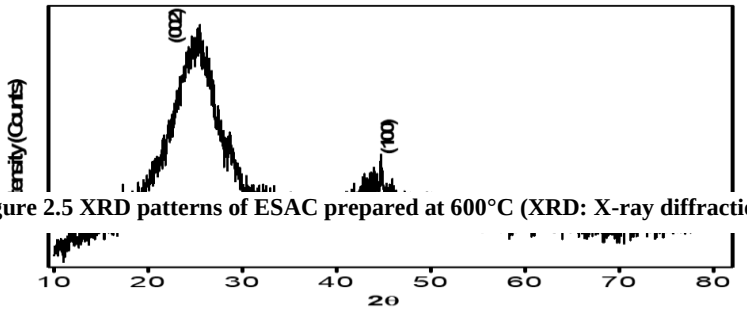


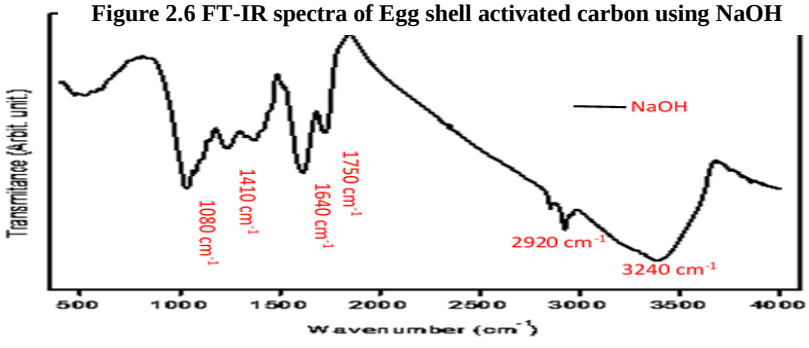
Figure 2.5 XRD patterns of ESAC prepared at 600°C (XRD: X-ray diffraction)

Additionally, minor XRD peaks at angles such as 31.5°, 40.5°, 50.2°, 54°, and 57.5° are attributed to residual inorganic compounds like calcium oxide (CaO), formed from the thermal degradation of calcium carbonate ($CaCO_3$) originally present in the eggshell. The combination of crystalline (graphitic) and amorphous phases, along with residual inorganic content, confirms the effective conversion of organic material to activated carbon [37]. This mixed-phase structure enhances the material's suitability for adsorption and catalytic applications, as it combines high surface area, porosity, and chemical stability.

c. **Fourier Transform Infrared Spectroscopy (FTIR)**

The application of FTIR analysis enables identification of surface functional groups on ESAC that contribute significantly to its adsorptive performance [38]. Spectral data reveal the presence of hydroxyl (O–H), carbonyl (C=O), carbon-oxygen (C–O), and carbonate (CO_3^{2-}) functionalities, evidenced by distinct absorption peaks: a broad band near 3420 cm^{-1} for hydroxyl groups, prominent signals at 1080 cm^{-1} for C–O bonds, around 1410 cm^{-1} for carbonate species, and at 1640 cm^{-1} and 1750 cm^{-1} for carbonyl moieties. These chemical groups establish reactive sites enabling hydrogen bonding, electrostatic forces, and dipole interactions that collectively enhance the material's capacity to extract diverse pollutants from aqueous media.

Figure 2.6 FT-IR spectra of Egg shell activated carbon using NaOH



The FTIR analysis also shows shifts, broadening, and the appearance or disappearance of peaks after activation, indicating chemical modifications that improve adsorption performance [39]. The presence of aliphatic C–H bonds (2920 cm^{-1}) and metal-oxygen bonds in the fingerprint region further contribute to the surface polarity and interaction potential of ESAC. The abundance and diversity of these surface functional groups, particularly hydroxyl and carbonyl groups, make eggshell activated carbon highly effective for water treatment applications, especially in adsorbing heavy metals, polar contaminants, and organic compounds from industrial wastewater.

d. **Brunauer-Emmett-Teller (BET)**

BET analysis represents an essential characterization method for eggshell-based activated carbon, yielding quantitative measurements of surface area, pore volume, and pore size distribution that directly influence adsorption capacity. The technique utilizes nitrogen adsorption isotherms obtained at cryogenic temperatures to

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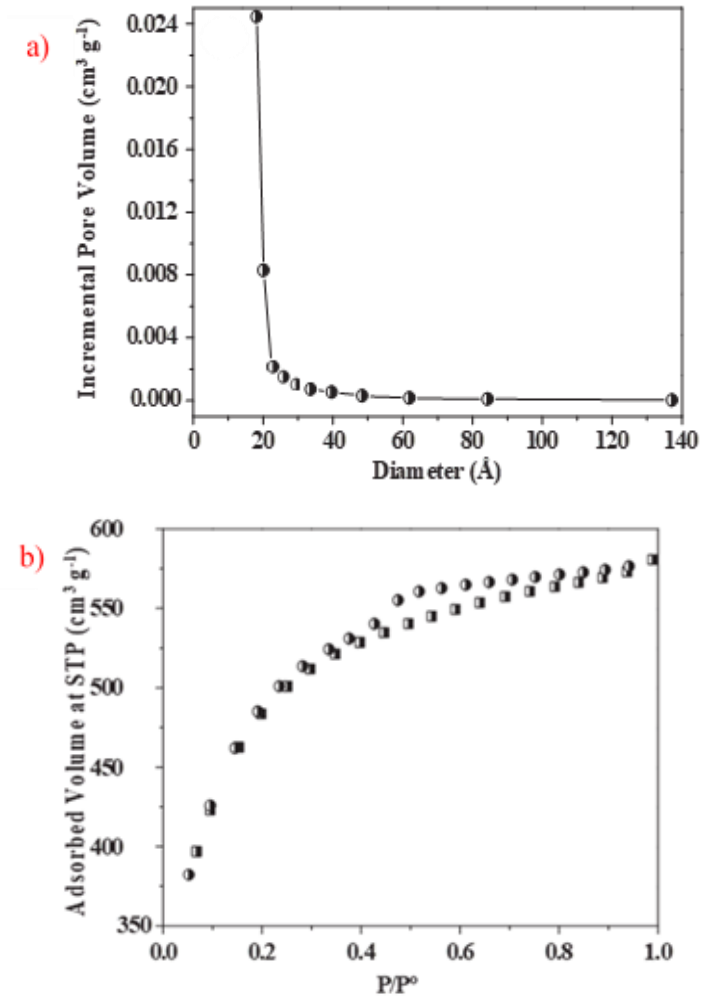

Figure 2.8 Nitrogen adsorption–desorption isotherms for prepared activated carbons with standard temperature and pressure (STP)

The material displays Type IV nitrogen adsorption-desorption isotherms characterized by marked hysteresis loops associated with mesoporous materials, while steep gas uptake at low relative pressures verifies significant micropore presence [45,46]. The eggshell-derived activated carbon demonstrates a high BET surface area of 786 m²/g, a total pore volume of 1.08 cm³/g, and an average pore diameter of 1.98 nm, with micropores accounting for the majority of the pore volume (0.82 cm³/g) and mesopores contributing 0.16 cm³/g. These properties confirm that the material is highly suitable for adsorption-based applications, particularly in water and wastewater treatment.

Figure 2.7 A graph plotting Incremental Pore Volume (in cm³/g) versus Pore Diameter (in Ångströms, Å)

Figure 2.9: summary of text-based data reporting key physical properties of ESAC porous material, according to standardized measurement protocols.

BET surface area (m2 g−1)	786 (500–2000 m²/g ISO 9277:2010)
Total pore volume (cm3 g−1)	1.08 (0.3 to 2.0 cm³/g ISO 15901-1:2005)
Micropore volume (cm3 g−1)	0.82 (0.2 to 1.0 cm³/g ISO 15901-1:2005)
Mesopore volume (cm3 g−1)	0.16 (0.1 to 1.0 cm³/g ISO 15901-1:2005)
Pore diameter (nm)	1.98

determine specific surface area (SBET). Complementary approaches including the Dubinin–Radushkevich and Barrett–Joyner–Halenda methods enable estimation of micropore and mesopore contributions and pore size profiling, respectively [40-44]. Pore distribution data indicate that ESAC possesses predominantly small pores (below 20 Å diameter), with maximum incremental pore volume reaching approximately 0.024 cm³/g. Beyond this threshold, incremental volume decreases dramatically, demonstrating minimal mesopore and macropore content. This micropore-dominant architecture enhances adsorption performance by maximizing the concentration of binding sites available for contaminant capture.

3. Results and Discussion

a. Adsorption efficiency of ESAC on Lead and Nickel

ESAC's capacity for lead and nickel removal from wastewater is evaluated through batch testing involving 50 mL metal solutions (e.g., 100 mg/L) with pH modification (2–10) using dilute HNO_3 or NaOH and addition of weighed adsorbent amounts (0.010–0.8 g). Sonication at room temperature for 5–180 minutes promotes adsorption, after which centrifugation at 2000 rpm for 3 minutes separates the solid phase. Residual metal concentrations are determined, and uptake capacity (q_e, mg/g) is calculated using $q_e = (C_o–C_e)V/m$, incorporating initial concentration (C_o), equilibrium concentration (C_e), volume (V), and mass (m) [45]. Percentage removal (%RE) follows $((C_o–C_e)/C_o) \times 100$, with operational parameters—pH, pollutant level, adsorbent quantity, and treatment duration—optimized for maximum lead and nickel extraction from Vrishabhavathi river industrial effluent samples [46]. Investigations employed variable contact times (4–28 hours), dosages (10–25 g/L), concentrations (10–50 mg/L), and pH levels (2–9).

i. Effect of adsorbent dosage

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Investigation of adsorbent loading effects on lead and nickel removal employed doses spanning 0.1 to 2.5 g. For lead, extraction efficiency rose significantly from 30% (0.1 g) to 79% (1 g), recording intermediate values of 41%, 52%, and 63% at 0.3 g, 0.5 g, and 0.8 g respectively. Dosages exceeding 1 g (1.5 g, 2 g, 2.5 g) produced only slight gains, with performance leveling at approximately 80%, demonstrating that equilibrium had been achieved and that further adsorbent additions did not meaningfully enhance active site accessibility. Similarly, nickel removal efficiency rose from 24% at 0.1 g to 63% at 1 g, with intermediate efficiencies of 36%, 44%, and 56% at 0.3 g, 0.5 g, and 0.8 g, respectively. Beyond 1 g, the removal efficiency plateaued around 64–65%, showing minimal gains despite further increases in adsorbent dosage. This trend reflects the saturation of adsorption sites and equilibrium attainment in the system. These results demonstrate that increasing adsorbent dosage enhances metal ion removal by providing more active sites up to an optimal dosage of 1 g for both lead and nickel. At this dosage, high removal efficiencies (79% for lead and 63% for nickel) are achieved while avoiding unnecessary excess adsorbent use, balancing effective contaminant removal with economic feasibility

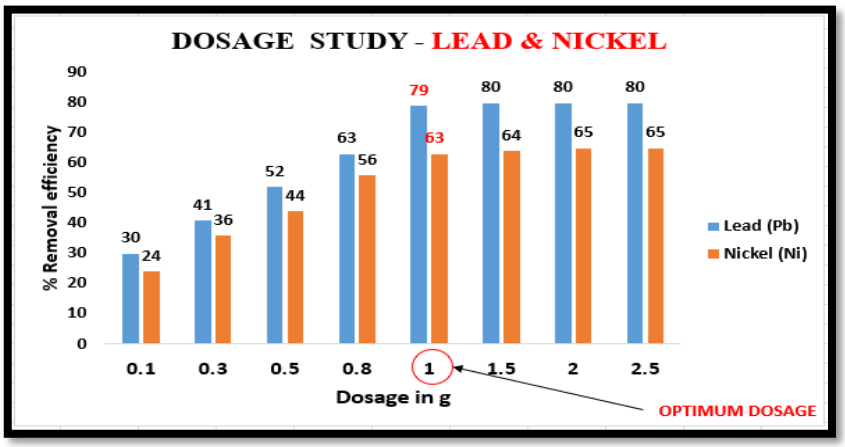

Figure 3.1 Graphical representation on the effect of Adsorbent Dosage on adsorption efficiency

Effect of contact time

Contact time influence on lead and nickel adsorption was investigated at 25±2°C using 1 g adsorbent at pH 6, with variable lead concentrations (10–50 mg/L) and constant nickel levels. Lead removal progressively increased from 38% (4 hours) to 79% (20 hours), peaking at 80% by 24 hours. Further extension beyond 24 hours produced no meaningful enhancement, confirming equilibrium attainment. The adsorption process displayed biphasic kinetics: initially rapid uptake facilitated by plentiful vacant sites, transitioning to slower rates as site occupancy approached saturation. Nickel exhibited comparable behavior, with removal rising sharply from 21% (4 hours) to 40% (12 hours), then more gradually to 63% (24 hours) before stabilizing near 64% (28 hours). Both metals demonstrated this two-stage pattern—fast initial binding followed by gradual equilibrium approach—reflecting progressive site saturation on ESAC. Consequently, 24 hours emerged as the optimal duration for batch experiments, achieving maximum removal (80% Pb, 63% Ni) while maintaining practical feasibility. Additional agitation time offered negligible benefit, establishing 24 hours as both effective and economically sensible for heavy metal treatment using ESAC.

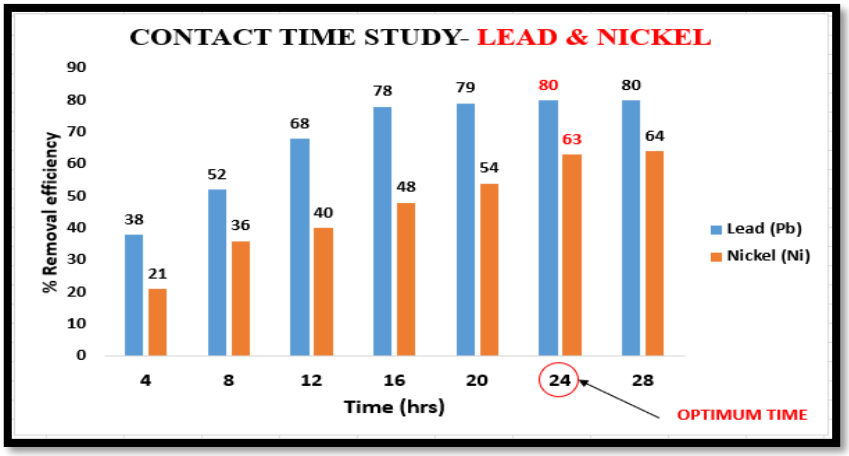

Figure 3.2 Graphical representation on the effect of Contact time on adsorption efficiency

ii. **Effect of pH**

Investigation into pH effects on lead and nickel adsorption demonstrates that solution acidity significantly governs heavy metal extraction from water. Lead removal exhibited an increase from 42% under strongly acidic conditions (pH 2) to an optimum of 80% at pH 6. Under highly acidic conditions (pH 2–3), excessive protons compete with Pb^{2+} for binding sites, suppressing metal uptake. As acidity decreases toward pH 4–6, diminished proton competition and strengthened electrostatic interactions between the anionic adsorbent surface and cationic lead species enhance removal performance to 80%. Above pH 6, efficiency diminishes as lead precipitates as hydroxide ($Pb(OH)_2$) and surface charge modifications reduce site availability.

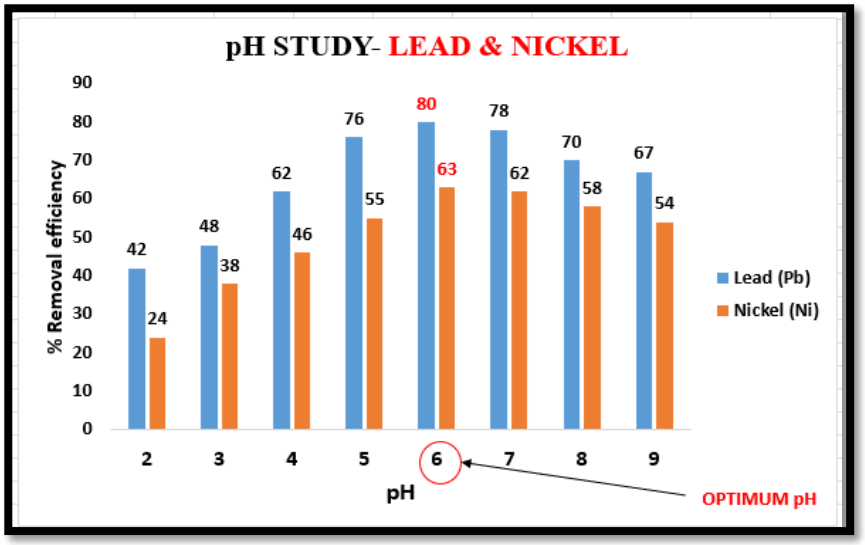

Figure 3.3 Graphical representation on the effect of pH on adsorption efficiency

In parallel, nickel extraction efficiency progressed from 24% at pH 2 to peak performance of 63% at pH 6 under defined conditions. Acidic conditions promote competition between hydrogen and nickel ions for available sites, constraining metal uptake. As acidity decreases, competitive interference lessens and surface electronegativity increases, facilitating stronger electrostatic binding and elevated nickel adsorption, recording 38%, 46%, and 55% at pH values of 3, 4, and 5, respectively. Beyond pH 6, nickel removal slightly decreases to 62%, 58%, and 54% at pH 7, 8, and 9, respectively, due to nickel hydroxide precipitation ($Ni(OH)_2$) and reduced active site availability. Overall, the findings

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demonstrate that mildly acidic conditions near pH 6 optimize adsorption for both lead and nickel by balancing reduced hydrogen ion competition and minimizing metal hydroxide precipitation. Controlling the solution pH is therefore essential to maximize adsorption efficiency and ensure effective removal of heavy metals in water treatment processes.

iii. Effect of Pollutant concentration

The effect of initial pollutant concentration on the adsorption efficiencies of lead and nickel was examined by varying their concentrations from 10 to 50 mg/L under constant conditions of temperature, pH, agitation speed, contact time, and adsorbent dose. For lead, removal efficiency increased from 69% at 10 mg/L to a peak of 79% at 20 mg/L, indicating an optimal balance between lead ion availability and active adsorption sites. At this concentration, the adsorbent effectively captures the maximum proportion of lead ions. Beyond 20 mg/L, lead removal efficiency declined progressively to 68% at 30 mg/L, 55% at 40 mg/L, and 51% at 50 mg/L. This reduction is attributed to the saturation of adsorption sites, where the number of lead ions exceeds the adsorbent's capacity, limiting further uptake despite increased pollutant concentration. Nickel adsorption followed a similar trend, rising from 58% at 10 mg/L to a maximum of 62% at 20 mg/L, then decreasing to 49%, 46%, and 39% at 30, 40, and 50 mg/L, respectively, due to site saturation. These results highlight the critical influence of initial pollutant concentration on adsorption efficiency, where low to moderate concentrations allow effective utilization of active sites, while higher concentrations overwhelm the adsorbent, reducing percentage removal. Thus, optimizing the starting concentration of contaminants proves essential for obtaining maximum adsorption effectiveness and reliable metal ion removal in applied wastewater treatment processes.

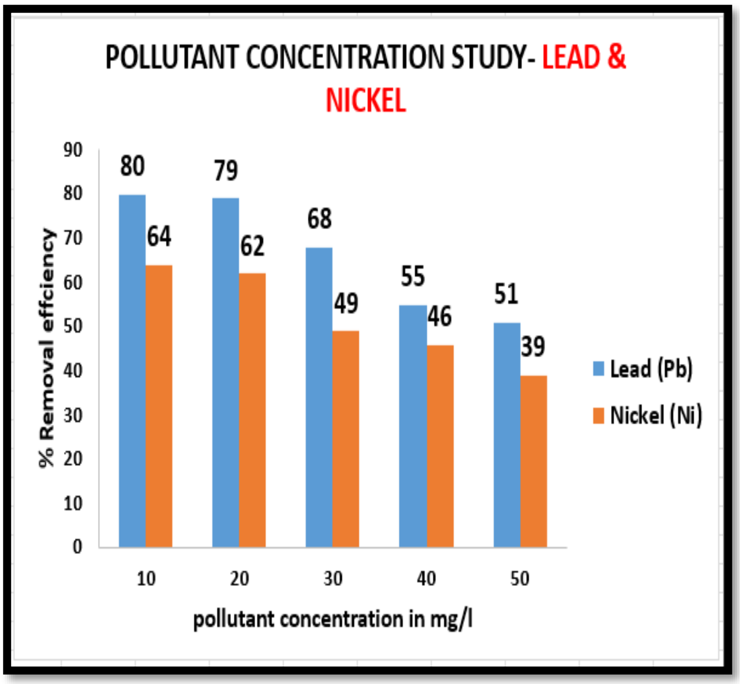

Figure 3.4 Graphical representation on the effect of Pollutant concentration on adsorption efficiency

From the real time sample, the ESAC managed to remove about 73% for lead and 56% for nickel, and CAC the efficiency removal was 67% for lead and 56% for nickel. Given these results, the material demonstrates promise for real-world applications, including the treatment of heavy metal-contaminated industrial effluents and commercial-scale use.

b. Adsorption mechanism

Isotherm models establish the connection between metal ion loading on ESAC and solution equilibrium concentrations, revealing fundamental adsorption characteristics. Studies examining ESAC performance frequently apply Langmuir, Freundlich, or Dubinin-Radushkevich frameworks [47-49]. The Dubinin-Radushkevich approach has demonstrated strong correlation with metal adsorption data for eggshell-derived adsorbents, pointing to heterogeneous surfaces where pore-filling dominates. These models quantify binding capacity and distinguish between monolayer (Langmuir) versus multilayer heterogeneous adsorption (Freundlich), essential for optimizing Cd^{2+}, Pb^{2+}, Ni^{2+}, and Zn^{2+} removal from wastewater.The binding mechanisms identified through isotherm studies encompass ion exchange, complexation, electrostatic interaction, and chelation between metal ions and surface groups on ESAC. Oxygen-containing functionalities (hydroxyl, carboxyl, carbonyl) introduced during preparation facilitate metal binding via complexation and exchange. Porosity and surface area also enable physical adsorption. Chemical modifications through acid/base treatment intensify functional group presence, markedly enhancing uptake capacity. Freundlich and Langmuir models are most frequently used to analyze experimental isotherms and were both implemented in this work.

Langmuir isotherm model

According to the Langmuir theory, adsorption proceeds as monolayer formation on a uniform surface containing a fixed number of sites, with the assumption that no lateral interactions occur between adsorbed species. The Langmuir expression establishes the connection between equilibrium adsorption capacity on the adsorbent (qe) and equilibrium adsorbate concentration in solution (Ce) as follows:

$$q_e = \frac{K_L b C_e}{1 + bC_e} \dots\dots\dots\dots\dots\dots\dots\dots 1$$

In this expression, KL and b represent Langmuir parameters, with KL indicating the maximum uptake capacity of the adsorbent and b reflecting the binding energy related to adsorption enthalpy [50]. A key characteristic of the Langmuir model is the dimensionless separation factor or equilibrium parameter (R_L), which reveals the favourability of the adsorption process.

$$R_L = \frac{1}{1 + K_L C_o} \dots\dots\dots\dots\dots\dots\dots\dots 2$$

When R_L falls between 0 and 1, the adsorption is advantageous. When identifying the type of adsorption, the value of R_L is more reliable. Adsorption is irreversible if $R_L = 0$ or linear if $R_L = 1$, unsatisfactory if $R_L > 1$, and satisfactory if $0 < R_L < 1$ [51].

i. Freundlich isotherm model

Freundlich isotherm theory describes adsorption on non-homogeneous adsorbent surfaces where adsorbate molecules form multiple layers and interact with each other. The mathematical relationship connecting equilibrium adsorption capacity, qe (mg/g), with equilibrium solution concentration of metal ions, Ce (mg/L), is expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \dots\dots\dots\dots\dots\dots\dots\dots 3$$

where the intercept ln k represents the adsorbent's capacity, while the slope 1/n reflects the adsorption intensity. The constant k depends on both temperature and the physicochemical characteristics of the adsorbent material. The exponent "n" reflects adsorption intensity variation and quantifies the degree of non-linearity in the adsorption process. Values of n exceeding 1 indicate favorable adsorption, while n < 1 suggests poor adsorption efficiency. The commonly encountered scenario of n > 1 can result from multiple factors including heterogeneous surface site distribution or conditions that weaken adsorbent-adsorbate interactions as surface loading increases [52,53].

The values of K_L and q_m are estimated from the graph of C_e/q_e versus C_e. (**Figure 3.4 Pb, Ni**), and the results are presented in **Tables 3.1 and 3.2**.

Table 2.1 Freundlich and Langmuir Constants for adsorption of Lead (Pb)

Adsorbate	Freundlich constants			Langmuir constants		
	n	K_F (mg/g) (L/mg)$^{1/n}$	R^2	K_L (L/g)	a_L (L/mg)	R^2
Lead (Pb)	1.20	0.250	0.995	0.160	0.0035	0.97

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Table 3.2 Freundlich and Langmuir Constants for adsorption of Nickel (Ni)

Adsorbate	Freundlich constants			Langmuir constants		
	n	K_F (mg/g) $(L/mg)^{1/n}$	R^2	K_L (L/g)	a_L (L/mg)	R^2
Nickel (Ni)	1.10	0.210	0.990	0.140	0.0030	0.96

The RL values in Table 3.3 reveal that eggshell powder exhibits favorable properties for capturing Pb and Ni ions. Regression coefficient (R2) analysis shows the Freundlich model better describes the removal process for both metals, with strong correspondence between experimental data and model predictions [54]. This aligns with prior research identifying the Freundlich framework as optimal for characterizing Pb and Ni binding mechanisms. Freundlich isotherm analysis (Figure 3.3) enables calculation of KF and n parameters from the slope and intercept of the ln Ce versus ln qe relationship, with resulting values shown in Table 3.1. The high R2 values (above 0.9) for both metal isotherms confirm this model accurately represents the equilibrium relationship between contaminant concentration in industrial effluent and ESAC uptake capacity [55-57]. Additionally, n values ranging between 1 and 10 verify that adsorption of both metals onto eggshell-based activated carbon proceeds under favorable conditions.

Table 3.3 Separation factor, RL values for the Lead (Pb) and Nickel (Ni) adsorption [58]

C_0 (mg/L)	R_L	
	Lead (Pb)	Nickel (Ni)
50	0.571	0.667
100	0.400	0.500
150	0.308	0.400
200	0.250	0.333

Table 3.3 Cost build-up for ESAC cost

S. No.	Items	Cost (INR)	
1	Eggshell collection, transportation and storage	10	
2	Chemicals	200	
3	Instruments	100	
4	Man power	50	
5	Miscellaneous		10
Total cost incurred			370
Total quantity of ESAC prepared			500g
Cost per gram			0.75

c. **Cost benefit analysis**

From the calculations done on building up the rate, the cost for the ESAC- 370/= INR- 500g is less compared to the costs of commercially activated carbon, which is 799/= INR- 500g. This significant price difference suggests that ESAC offers a cost-effective alternative as an adsorbent material. Choosing ESAC can reduce overall treatment expenses while maintaining adsorption performance, making it a financially advantageous option for water purification or pollutant removal processes.

4. Conclusion

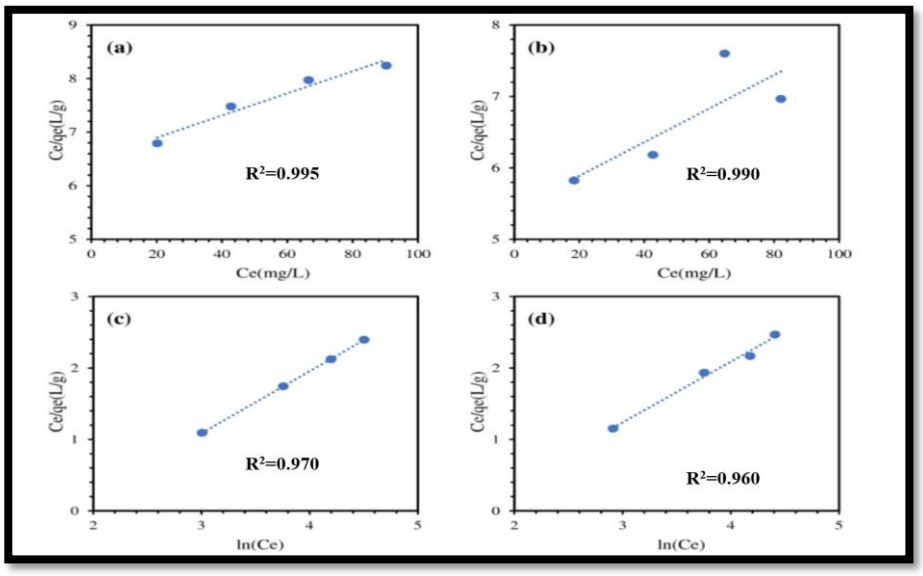

Figure 3. 5 Langmuir model plot for the adsorption of (a) Pb and (b) Ni ion, and Freundlich model plot for the adsorption of (c) Pb and (d) Ni ion using eggshell activated carbon

In summary, this work validates eggshell-derived activated carbon as an attractive, low-cost, and eco-friendly material for remediating lead and nickel contamination in industrial wastewater, specifically addressing pollution challenges in areas like Karnataka's Vrishabhavathi River. The research aimed to determine ESAC's removal capacity for Pb and Ni while examining how factors such as pH, adsorbent quantity, reaction time, and initial metal concentrations influence performance. Material analysis using SEM, XRD, FTIR, and BET revealed key structural features including high porosity, substantial specific surface area, and abundant surface functionalities critical for adsorption. Experimental results identified optimal operating conditions as pH approximately 6, dosage around 1 g, and contact time of 24 hours, yielding effective Pb and Ni removal. These findings align with the study's objective to introduce a locally available, low-cost alternative to conventional adsorbents for heavy metal remediation. The research confirms that ESAC delivers high removal efficiencies (up to 80% for Pb and 63% for Ni), and its use leverages agro-waste valorization while helping to address serious environmental threats from industrial effluent. The practical applicability of ESAC is supported by its robust performance across a range of wastewater conditions and its ease of synthesis, supporting the potential for scaled deployment in water-scarce, economically constrained contexts.

However, the study also identifies areas requiring further investigation to fully establish ESAC's viability for large-scale use. Future research should focus on pilot-to-industrial scale trials to assess regeneration, reuse, and lifecycle performance of ESAC in continuous treatment systems. Comparative studies evaluating ESAC against different commercial adsorbents under identical, real-world effluent flows will help refine cost-benefit analysis and operational guidance. Additionally, exploration of surface modifications and composite formulations could enhance adsorption selectivity and efficiency for a broader range of contaminants. These directions will support the ultimate goal of integrating eggshell-based adsorbents into comprehensive, sustainable water treatment strategies for industrial regions worldwide.

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