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Article

Effectiveness of HCl-Activated Duck Eggshell (*Anas platyrhynchos domesticus*) for Pb^{2+} Removal from Well Water

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Abstract. Clean water is essential for human health; however, Pb^{2+} contamination in well water remains a serious environmental concern, particularly in areas with industrial activities and inadequate waste management. Conventional water treatment methods are often costly and require complex infrastructure, creating the need for affordable and environmentally friendly alternatives. This study investigated the effectiveness of HCl-activated eggshells as an adsorbent for Pb^{2+} removal from well water. Eggshells were cleaned, chemically activated with hydrochloric acid (HCl), and applied to well water samples. A 2 g adsorbent dose was used with a contact time of 1 hour, and the eggshells were activated using 0.5 M HCl. Pb^{2+} concentrations were measured using Atomic Absorption Spectrophotometry (AAS). The initial Pb^{2+} concentration of 0.0335 mg/L decreased to 0.0310 mg/L after treatment with non-activated eggshells (7.46% removal), while HCl-activated eggshells reduced the concentration to 0.0109 mg/L (67.46% removal). These results demonstrate that HCl activation significantly enhances the adsorption capacity of eggshells for Pb^{2+} removal. The final Pb^{2+} concentration of 0.0109 mg/L was below the 0.03 mg/L threshold for well water, indicating that HCl-activated eggshells were effective in reducing Pb^{2+} contamination. However, this value remains slightly above the 0.01 mg/L drinking water limit; therefore, further treatment or optimization may be required if the treated water is intended for direct consumption.

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1. Introduction

Groundwater from wells is one of the primary sources of clean water, particularly in rural areas and regions lacking piped water supply [1-2]. However, its quality is highly vulnerable to contamination by heavy metals originating from industrial effluents, agricultural activities, domestic waste, mining operations, and the corrosion of metal-containing materials [3-4]. Among these contaminants, lead (Pb^{2+}) is of particular concern because of its persistence, toxicity, and tendency to accumulate in the human body, where it can cause neurological disorders, kidney damage, anemia, developmental impairment in children, and reproductive problems in adults [5–7]. Consequently, both the World Health Organization (WHO) and the Indonesian Ministry of Health have established a maximum permissible Pb concentration of 0.01 mg/L in drinking water [8-9].

Various technologies have been developed to remove heavy metals from contaminated water, including chemical precipitation, coagulation–flocculation, membrane filtration, and biological treatment [10–12]. Among these methods, adsorption has gained considerable attention because of its simplicity, cost-effectiveness, and high removal efficiency, particularly when low-cost natural adsorbents are used [13–15].

Duck eggshells (*Anas platyrhynchos domesticus*) are an abundant organic waste composed of more than 90% calcium carbonate ($CaCO_3$), making them a promising adsorbent for heavy metal removal [16-17]. Their porous structure enables Pb^{2+} adsorption through ion exchange and surface precipitation mechanisms [18-19]. Previous studies have demonstrated the potential of eggshell-based adsorbents for removing heavy metals from wastewater, offering an inexpensive and environmentally friendly alternative to conventional materials [16].

Chemical activation with hydrochloric acid (HCl) [20] is widely used to enhance the adsorption performance of $CaCO_3$-based materials [20]. HCl partially dissolves the mineral matrix, creating additional pores and increasing the number of active adsorption sites, thereby improving metal uptake [21,22]. As summarized in Table 1, previous studies have demonstrated the potential of chicken and duck eggshells for heavy metal removal, including Pb^{2+}. However, most studies have focused on chicken eggshells, modified eggshell materials, or controlled wastewater and laboratory conditions. The application of HCl-activated duck eggshells for Pb^{2+} removal from naturally occurring well water has received limited attention. In particular, the performance of this adsorbent in a real well-water matrix, which may contain various dissolved ions and other components that can affect Pb^{2+} adsorption, remains insufficiently investigated. This represents an important research gap for assessing the practical applicability of eggshell-based adsorbents for community water treatment.

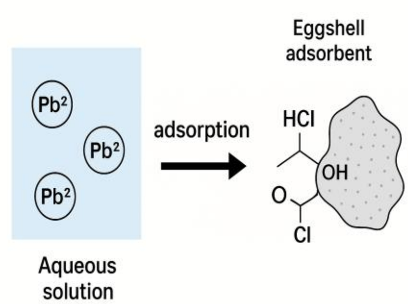

Figure 1. Mechanism of Pb^{2+} Adsorption by Eggshell Adsorbents

Table 1. Previous Studies on Eggshell Waste-Based Adsorbents

No.	Eggshell Type and Treatment	Target Heavy Metal	Results / Removal Efficiency	Reference
1	Chicken eggshell, activated with 0.1 M HCl	Pb^{2+}, Cd^{2+}	High Pb^{2+} removal efficiency (using 9 g of adsorbent) and Cd^{2+} removal efficiency approaching 100%	[23]
2	Chicken eggshell (activated carbon/eggshell powder)	Pb^{2+}	Pb^{2+} removal efficiency of approximately 48.21% following chemical activation	[7]
3	Modified chicken eggshell (eggshell/Ag–Fe nanocomposite)	Pb^{2+}, As^{5+}, Hg^{2+}	Pb^{2+} adsorption capacity of 3.90 mg/g; significant adsorption of As^{5+} and Hg^{2+}, indicating the high potential of modified eggshell adsorbents	[24]
4	Chicken eggshell activated with acid/base (including HCl)	Cu^{2+}	Optimum Cu^{2+} adsorption at pH ~6, 60 min contact time, and 0.25 g adsorbent dosage	[20]
5	Chicken eggshell biosorbent (with or without treatment)	Pb^{2+}, Cd^{2+}	Maximum removal efficiencies of 65.99% for Pb^{2+} and 93.16% for Cd^{2+} under optimum conditions	[25]
6	Duck and chicken eggshells (comparative bioadsorbents)	Fe	Effective adsorption of Fe from industrial wastewater, demonstrating the potential of duck and chicken eggshells as bioadsorbents	[26]

Therefore, this study aimed to investigate the adsorption performance of HCl-activated duck eggshells in reducing Pb^{2+} concentrations in well water and to evaluate their potential as an affordable and sustainable filtration material for community water treatment. It was hypothesized that HCl activation would enhance the adsorption performance of duck eggshells toward Pb^{2+} in well water, resulting in a greater reduction in Pb^{2+} concentration compared with untreated eggshells.

2. Experimental Section

2.1. Materials

Duck eggshells (*Anas platyrhynchos domesticus*) were collected as the primary adsorbent material. Hydrochloric acid (HCl, 0.5 M) was used as the chemical activating agent, while distilled water was used for washing the adsorbent after activation. Well water samples were collected from the selected sampling site for adsorption experiments. A mild detergent was used to remove impurities from the eggshell surface during the cleaning process. The concentration of Pb^{2+} in the well water samples before and after treatment was determined using an Atomic Absorption Spectrophotometer (AAS) *spectra 3000* and surface morphology of the adsorbent before and after HCl activation was characterized using a *Scanning Electron Microscope* (SEM).

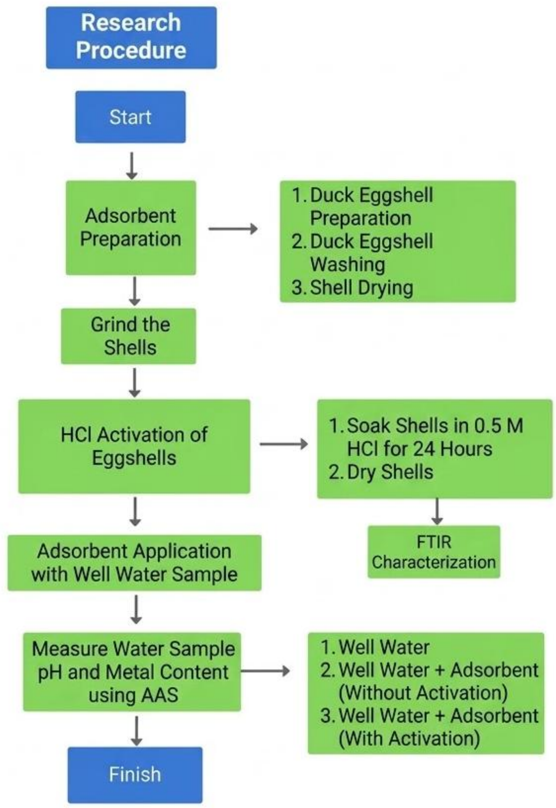

Figure 2. Schematic/Flowchart of research

2.2. Method

2.2.1 Adsorbent Preparation

Duck eggshells (*Anas platyrhynchos domesticus*) were collected, and the inner membrane and adhering impurities were removed. The eggshells were thoroughly rinsed with running water, briefly washed with a mild detergent solution, and rinsed again with distilled water. The cleaned eggshells were dried at 60–105 °C for 1 hour, until a constant weight was obtained and then ground into a fine powder for use as the adsorbent.

2.2.2. HCl Activation of Eggshell Adsorbent

A 0.5 M hydrochloric acid (HCl) solution was prepared as the activating agent. Fifty grams of eggshell powder were immersed in 250 mL of the HCl solution and stirred intermittently to ensure uniform contact. The suspension was allowed to stand at room temperature for approximately 24 h. After activation, the adsorbent was repeatedly washed with distilled water until free of residual acid, dried completely, and stored in labeled containers prior to use.

2.2.3. Adsorption Experiment

A total of 100 mL of well water sample collected from the Lubuk Buaya area, Padang City, West Sumatra, Indonesia in a beaker, and 2 g of the prepared adsorbent was added. The mixture was stirred for approximately 1 h to facilitate adsorption. The treated water was subsequently filtered, and the residual Pb^{2+} concentration was determined using Atomic Absorption Spectrophotometry (AAS).

3. Results and Discussion

3.1. Visual Characterization

Visual characterization showed that the untreated duck eggshell powder had a bluish-white appearance. Following thermal treatment and HCl activation, the adsorbent changed to an off-white to light gray color. This color change indicates the partial removal of surface impurities and mineral modification during the activation process, which is commonly associated with an increase in surface porosity and the formation of additional active adsorption sites.

Figure 3. Eggshell-Derived Adsorbent Powder

The observed color change indicates alterations in the physical characteristics of the material resulting from the removal of moisture, organic compounds, and surface impurities. In addition, the HCl activation process is presumed to increase pore accessibility and surface area, thereby enhancing the adsorption capacity of the adsorbent for Pb^{2+} ions [17].

3.2. Fourier Transform Infrared (FTIR) Characterization

Fourier Transform Infrared (FTIR) spectroscopy was performed to identify and compare the functional groups present on the eggshell adsorbent before and after HCl activation. The FTIR spectra of the untreated and HCl-activated eggshell adsorbents are presented in the following figure 4.

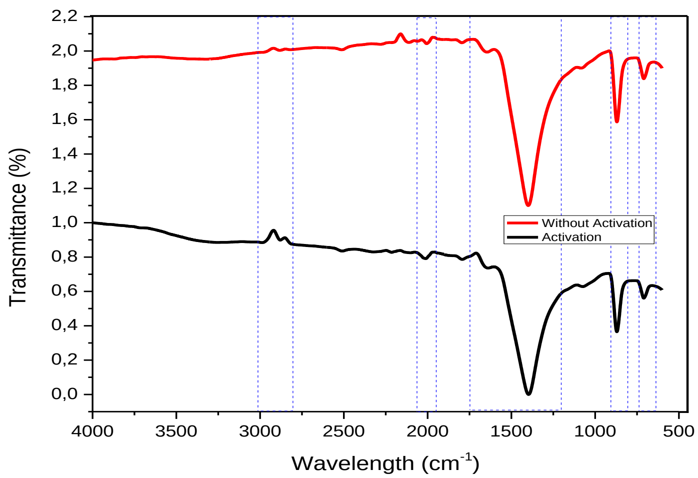

Figure 4. FTIR Spectrum of the Adsorbent

Based on the FTIR spectra, several characteristic absorption bands were observed for both the untreated and HCl-activated eggshell adsorbents, indicating the presence of typical functional groups [22]. Differences in the intensity and shape of these absorption bands suggest that HCl activation altered the surface chemical characteristics of the adsorbent. The identified functional groups and their corresponding assignments are summarized in the following table 2.

Table 2. FTIR Absorption Bands of the Eggshell Adsorbent

Wavenumber (cm^{-1})	Functional Groups	Intensity	Interpretation
3400–3200	O–H stretching	Weak	Indicates the presence of hydroxyl (O–H) groups or water molecules adsorbed on the surface of the adsorbent.
2920–2850	C–H stretching	Strong	Attributed to residual organic compounds from the eggshell membrane, such as proteins or lipids.
2100–1900	Carbonate Combination Vibration	Weak	Generally associated with the combination vibration of carbonate ions (CO_3^{2-}) in calcium carbonate ($CaCO_3$).
1450–1410	C–O asymmetric stretching (CO_3^{2-})	Strong	Characteristic absorption band of calcium carbonate ($CaCO_3$), confirming the presence of carbonate ions as the primary component of the eggshell.
1080–1000	C–O stretching	Weak	Attributed to the C–O stretching vibration of carbonate groups or oxygen-containing functional groups on the adsorbent surface.
875–870	Out-of-plane bending CO_3^{2-}	Strong	Characteristic absorption band of calcite ($CaCO_3$).
715–710	In-plane bending CO_3^{2-}	Strong	Another characteristic absorption band of crystalline calcium carbonate ($CaCO_3$).

Based on the FTIR characterization, the eggshell adsorbent exhibited the presence of hydroxyl (O–H), carbonate (CO_3^{2-}), and a small amount of organic C–H functional groups. The prominent absorption bands observed at approximately 1410–1450 cm^{-1}, 870 cm^{-1}, and 710 cm^{-1} confirmed that calcium carbonate ($CaCO_3$) in the calcite phase was the primary component of the adsorbent. Following HCl activation, changes in the intensity of several absorption bands were observed, indicating an increase in the number of active sites on the adsorbent surface. The activation process likely removed impurities blocking the adsorbent pores, thereby improving the accessibility of carbonate and hydroxyl groups for interaction with metal ions in solution [20],[27]. These functional groups play a crucial role in Pb^{2+} adsorption through electrostatic attraction, ion exchange, and surface complexation mechanisms [9],[22]. Therefore, the FTIR results support the adsorption findings, demonstrating that HCl activation enhanced the adsorption performance of the eggshell adsorbent.

3.3. Scanning Electron Microscopy (SEM)

The surface morphology of the eggshell adsorbent was characterized using Scanning Electron Microscopy (SEM). This analysis was conducted to examine the particle morphology, particle size, and surface texture, which may influence the adsorption capacity of the adsorbent toward Pb^{2+} ions. SEM observations were performed at magnifications of 50,000× and 100,000× to obtain detailed images of the adsorbent surface structure. The SEM micrographs of the eggshell adsorbent are presented in the following figure.

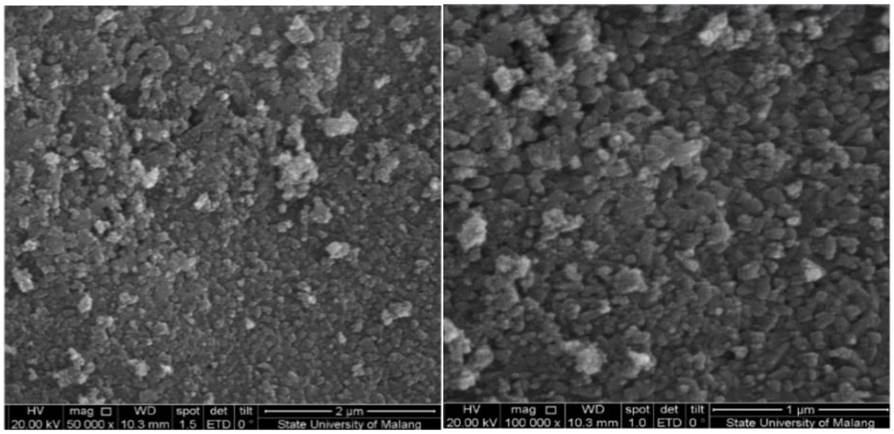

Figure 5. Surface morphology of the eggshell adsorbent observed by SEM at (a) 50,000× magnification and (b) 100,000× magnification.

The surface morphology of the eggshell adsorbent was characterized using Scanning Electron Microscopy (SEM) at magnifications of 50,000× and 100,000×. The SEM micrographs revealed that the adsorbent surface consisted of irregularly distributed micro- to submicron-sized particles forming agglomerated structures. At 50,000× magnification, the surface appeared relatively rough, with clusters of interconnected particles [28-29]. This morphology suggests a heterogeneous surface texture that may provide a relatively large contact area for the adsorption process.

At 100,000× magnification, the particle morphology became more distinct, showing densely packed fine particles aggregated into compact structures [30]. Small gaps between adjacent particles were also observed, indicating the presence of pores or interparticle spaces that could facilitate the diffusion of Pb^{2+} ions toward the active adsorption sites. Such a rough and porous surface is favorable for enhancing the adsorption of Pb^{2+} from aqueous solutions.

Overall, the SEM observations indicate that the eggshell adsorbent possesses a complex surface morphology with numerous potential active sites for adsorption. The presence of particle agglomerates and interparticle pores is likely to contribute to the improved adsorption performance of the adsorbent, particularly after HCl activation, resulting in a greater reduction of Pb^{2+} concentration in well water.

3.4. Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectroscopy (AAS) analysis was performed to determine the changes in Pb^{2+} concentration in well water before and after treatment with the eggshell adsorbent. Pb^{2+} concentrations were measured under three experimental conditions: untreated well water (control), well water treated with non-activated eggshell adsorbent, and well water treated with HCl-activated eggshell adsorbent. The Pb^{2+} concentrations obtained for these three samples are presented in the following table.

Table 3. Pb^{2+} Concentration in Well Water Samples Before and After Adsorbent Treatment

No	Sample Name	(mg/L)
1	Well Water	0.0335 ± 0.0061
2	Well Water + Adsorbent (before activation)	0.0310 ± 0.0046
3	Well Water + Adsorbent (after activation)	0.0109 ± 0.0061

Table 4. Percentage of Pb^{2+} Removal from Well Water After Adsorbent Treatment

No	Nama Sampel	% Pengurangan
1	Well Water + Adsorbent (before activation)	7.46
2	Well Water + Adsorbent (after activation)	67.46

The AAS results demonstrated that HCl activation significantly enhanced the ability of the eggshell adsorbent to remove Pb^{2+} from well water. The initial Pb^{2+} concentration in the well water sample was 0.0335 ± 0.0061 mg/L. Treatment with the non-activated adsorbent reduced the Pb^{2+} concentration to 0.0310 ± 0.0046 mg/L, corresponding to a removal efficiency of 7.46%. This relatively low removal efficiency indicates that the untreated adsorbent possessed a limited number of accessible active sites for Pb^{2+} adsorption [31]. In addition, surface impurities and blocked pores may have restricted the interaction between the adsorbent and Pb^{2+} ions, thereby limiting the adsorption process.

In contrast, the HCl-activated adsorbent exhibited substantially higher adsorption performance. The Pb^{2+} concentration decreased to 0.0109 ± 0.0061 mg/L, corresponding to a removal efficiency of 67.46%. These results indicate that HCl activation increased the adsorption efficiency by nearly ninefold compared with the non-activated adsorbent [10].

The enhanced adsorption performance is attributed to the modification of the adsorbent surface during HCl activation, including an increase in surface area, the development of additional pores, and the exposure of previously inaccessible active sites. These structural changes facilitate greater interaction between Pb^{2+} ions and the adsorbent surface, thereby improving Pb^{2+} removal. This finding is consistent with previous studies reporting that chemical activation of biomass-based adsorbents enhances adsorption capacity by increasing pore development and the availability of active adsorption sites.

4. Conclusion

FTIR characterization confirmed the presence of carbonate (CO_3^{2-}) and hydroxyl (O–H) functional groups on the eggshell adsorbent, which serve as potential active sites for Pb^{2+} adsorption. SEM analysis revealed a rough, agglomerated surface morphology with interparticle pores that increased the available contact area for adsorption. These structural and chemical characteristics contributed to the effective removal of Pb^{2+}, as confirmed by AAS analysis. The HCl-activated eggshell adsorbent reduced the Pb^{2+} concentration from 0.0335 mg/L to 0.0109 mg/L, achieving a removal efficiency of 67.46%, which was substantially higher than that of the non-activated adsorbent (7.46%).

The final Pb^{2+} concentration of 0.0109 mg/L was below the applicable threshold for well water of 0.03 mg/L, indicating that the treatment effectively reduced Pb^{2+} contamination in the well water. However, this value remained slightly above the WHO drinking-water guideline of 0.01 mg/L, indicating that further treatment or optimization would be necessary if the treated water is intended for direct consumption. These findings demonstrate that HCl activation effectively improves the physicochemical properties of eggshell adsorbents, making them a promising low-cost, environmentally friendly, and sustainable material for well water treatment.

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