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Impact of pH on the Removal of Cadmium (II) Ions from Aqueous Solution using Rice Husk Ash as Adsorbent

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Abstract

The removal of cadmium Cd (II) from aqueous solutions using rice husk ash (RHA) is fundamentally governed by the solution's pH, which modulates the electrostatic interactions at the adsorbent-metal interface. In highly acidic environments, a high concentration of hydrogen ions H^+ acts as a primary competitor for available binding sites, imparting a positive charge to the ash surface. This results in electrostatic repulsion of the positively charged cadmium ions, significantly hindering removal efficiency. As the pH increases toward neutrality, the reduction in H^+ competition facilitates the migration of Cd (II) ions toward the ash surface.
This study investigated Cd (II) adsorption as a function of equilibrium time, adsorbent dosage, initial metal concentration, pH, and particle size using a batch system. Results indicate that removal efficiency is positively correlated with increasing pH levels. Specifically, modified rice husk ash achieved a maximum adsorption capacity of 0.396 mg/g (76.27% removal) at an optimal pH of 7.5, a contact time of 140 minutes, and an initial concentration of 0.192 mg/L. The adsorption data demonstrated a strong fit for both Langmuir and Freundlich isotherms. Ultimately, the findings confirm that modified rice husk ash serves as a more favourable and effective adsorbent than unmodified RHA for cadmium remediation.

Keywords: Adsorption, Rice Husk Ash, Aqueous solution, modified and unmodified adsorbent.

Introduction

Accelerated industrial development has resulted in the release of significant volumes of metal-laden industrial wastewater and domestic wastewater into aquatic environments. The subsequent emerged as a critical environmental concern due to its toxicity and persistence emerged as a critical global environmental and public health crisis. Among these pollutants, cadmium Cd (II) is severe threats to ecological stability and human health hazardous elements high toxicity even at low concentrations extreme toxicity, prolonged biological half-life, and high potential for bioaccumulation within the food chain. Sanni & Singh (2022), Sarkar and Mridha (2023). Industrial activities including electroplating, battery manufacturing, pigment production, and mining frequently discharge elevated concentrations of cadmium into aquatic environments. Human exposure to even trace amounts severe physiological disorders and chronic toxicity in living organisms' severe health complications, most notably renal failure, bone degradation (such as Itai-Itai disease), and potential carcinogenic effects. Due to these significant risks, developing efficient, cost-effective methods for the remediation of Cd (II) a major environmental concern that demands immediate attention and remediation an urgent priority for environmental researchers. Feng *et al*. (2004), Das *et al* (2013), Ahamad *et al*. (2015), Bhowmick (2024), Dee and Mahata (2025).

Classical wastewater treatment techniques, conventional treatment modalities, including chemical precipitation and ion exchange, and membrane filtration-are frequently hindered by high operational costs, intensive energy requirements, and the production of secondary toxic sludge. In contrast, adsorption has evolved into a prominent sustainable alternative due to and green profile of the adsorbent materials compatibility with low-cost, non-conventional materials. Over the past decade, Argo-based residues, such as Rice Husk Ash (RHA) have been extensively researched as "green" adsorbents. RHA is characterized by its high silica content, porous architecture, and significant surface area, which collectively provide a high density of active binding sites for the effective sequestration of metal ions. Hegazi (2013), Li and wang (2024), Prasad and Mukherjee (2025).

The efficiency of the adsorption process is not static; it is profoundly influenced by the surface morphology and chemical attributes of the aqueous environment, with solution pH serving as the most critical variable. The pH level dictates the ionization state of the distribution of functional entities on the rice husk ash surface and determines the chemical speciation of cadmium in the solution. Consequently, understanding the precise relationship between pH levels and metal sequestration is essential for the optimization of treatment systems. This research aims to analyse how varying pH levels affect the surface charge of rice husk ash and its subsequent capacity for Cd (II) removal, providing a robust theoretical foundation for the large-scale application of this agricultural byproduct in environmental remediation. Mahvi (2004), Kumar *et al* (2006), Mane *et al*. (2007), Gupta and Nayak (2012), Mishra *et al* (2021), Anuradha Singh and S.K. Singh (2022).

Experimental Methods

The experimental procedure for removing Cd (II) eemploying Rice Husk Ash (RHA) as an. follows a systematic batch adsorption approach to evaluate both modified and unmodified forms. This methodology ensures that the influence of pH is isolated and accurately measured against the material's adsorption capacity. Initially, a standard stock solution of cadmium is prepared, and the pH is adjusted across a specific range using dilute HCl or NaOH. A fixed dosage of RHA is added to the solution, and the mixture is agitated in a batch shaker to maintain uniform contact between the metal ions and the adsorbent surface. After reaching the designated contact time, the adsorbent is separated via filtration, and the residual metal concentration is measured to calculate the percentage removal. This controlled process allows for a precise comparison of how surface modification enhances the efficiency of this agricultural byproduct.

1. **Preparation of the Agricultural Residue (Rice Husk Ash)**

To remove dust and inherent soluble impurities, the collected raw rice husk was extensively rinsed with deionized water until the washings reached clarity. Following the cleaning process, the husks were dried in a hot air oven at 105°C and subsequently subjected to controlled combustion in a muffle furnace at temperatures between 500°C and 700°C for several hours. The organic fraction is effectively volatilized during this thermal process, producing a. The produced Rice Husk Ash (RHA) was then ground and sieved to a uniform particle particle dimension, generally falling between 100 and 200 mesh, to ensure a consistent surface area for subsequent experimental procedures. The chemical properties of the prepared RHA are detailed in Table 1.

Table 1: Chemical Composition of Rice Husk Ash (RHA)

Component	Composition (% w/w of dry matter)
Silicon Dioxide (SiO_2)	91.35%
Aluminium Oxide (Al_2O_3)	1.83%
Iron (III) Oxide (Fe_2O_3)	2.51%
Calcium Oxide (CaO)	1.35%
Magnesium Oxide (MgO)	1.04%
Density (g/ce)	2.69
Loss on Ignition (LOI)	13.47%

(Adapted from Bansal and Sharma, 1992)

2. **Preparation of the Cadmium Solution (Adsorbate)**

A stock solution of Cadmium 1000mg/L is prepared by dissolving an accurate mass of analytical-grade cadmium nitrate or cadmium chloride ($CdCl_2$) in distilled water. This concentrated stock serves as the foundational precursor for all subsequent experimental dilutions, from which working solutions of varying concentrations e.g., 10 mg/L to 100 mg/L are precisely prepared. These solutions are utilized to evaluate the Cd (II) removal efficiency of both modified and unmodified rice husk ash by monitoring the reduction in metal concentration following treatment. This standardized preparation ensures that initial concentration variables are strictly controlled across all batch tests. Ultimately, this systematic methodology facilitates for a clear assessment of how chemical modification enhances the sequestering capabilities of the agricultural byproduct.

3. **pH Adjustment and Control**

To investigate the pH-dependent adsorption behavior of Cd (II) by rice husk ash, a series of identical cadmium solutions are prepared. The initial pH of each solution is precisely adjusted within a range of 2.0 to 10.0 using dilute hydrochloric acid (HCl) or sodium hydroxide (NaOH). A digital pH meter is employed to monitor these levels throughout the procedure, ensuring experimental accuracy. This systematic variation is of great importance, as it allows for the determination of the optimal chemical environment for maximum metal sequestration.

4. **Batch Adsorption Procedure**

The experiments are conducted in 250 ml Erlenmeyer flasks, where a fixed dosage of Rice Husk Ash-typically ranging from 0.5g to 2.0g per litter-is added to each cadmium-bearing solution. To maintain a controlled environment, these flasks are placed in a thermostatic shaker and agitated at a constant speed of 150–200 rpm. This continuous mechanical stirring is vital, as it facilitates uniform contact between the Cd (II) ions and the active binding sites on the adsorbent surface. The agitation period is carefully timed to ensure the system reaches a state of adsorption equilibrium. Once the designated contact time is completed, the samples are processed to separate the solid ash from the liquid phase. This standardized batch approach ensures consistent evaluation of how specific parameters influence the final metal removal efficiency.

5. **Adsorption Kinetics of Metals**

The study of adsorption kinetics for Cd (II) removal by rice husk ash across varying pH levels exerts a significant influence on the overall treatment process. While adsorption capacity defines the total quantity of metal ions the material can sequester, kinetics provides the essential timeline for the reaction, describing the specific rate at which ions migrate diffused from the fluid phase toward the solid adsorbent surface. This "how fast" component is a fundamental aspect of environmental modelling, as it dictates the required residence time for pollutants in a treatment system. Consequently, understanding these kinetic rates is indispensable for engineers designing large-scale, efficient industrial wastewater facilities, ensuring that the sequestration process reaches its maximum potential within a practical timeframe.

Adsorption equilibrium was evaluated by applying the Freundlich, Temkin and Langmuir isotherms models at various initial concentrations of the studied metal ions in the range of 20 - 100 mg/L. The amount of the metal adsorbed (qe) and the percentage metal ion removed (% adsorbed) for Cd (II)) the uptake of ions was quantitatively assessed by employing the following equations:

$$qe = \frac{V(Co - Ce)}{100M}$$

$$\% \text{ Adsorbed} = \frac{(Co - Ce)}{Co} x100$$

Where q e is the quantity of adsorbate ions retained per unit mass of adsorbent (mg/g); C_o and C_e are the initial and final (equilibrium) concentrations of the metal ions (mg/L); V is the total solution volume (mL); and M is the mass of the adsorbent dose (g).

To elucidate the rate-controlling mechanisms of adsorption, heavy metals generally follow three consecutive steps:

- **i). Film Diffusion:** The transport of metal ions from the bulk solution the bulk solution through a thin the external liquid film boundary layer particle
- **ii). Intra-particle Diffusion:** The migration of the ions into the internal pore network of the adsorbent.
- **iii). Adsorption:** The actual chemical or physical Sequestration of the metal ion at the reactive centers of the adsorbent matrix (Jaiswal and Singh (2023).

Table 2: Effect of pH on adsorption of Cd (II) by Rice husk ash (unmodified) at different pH.

Time (Min)	pH 5.5		pH 6.5		pH 7.5		pH 8.5	
	Amount adsorbed mg/g	Percentage of Adsorption	Amount adsorbed mg/g	Percentage of Adsorption	Amount adsorbed mg/g	Percentage of Adsorption	Amount adsorbed mg/g	Percentage of Adsorption
20	0.048	7.62	0.127	23.460	0.164	28.36	0.086	15.28
40	0.179	11.83	0.210	39.87	0.239	45.52	0.142	26.18
60	0.096	14.73	0.242	47.28	0.286	55.27	0.176	32.12
80	0.103	16.98	0.268	52.64	0.310	60.10	0.192	35.27
100	0.118	18.74	0.284	54.18	0.318	61.47	0.203	40.10
120	0.130	18.97	0.296	58.72	0.338	63.42	0.243	42.26
140	0.130	18.97	0.296	58.72	0.338	63.42	0.243	42.26

(Temp. 30.0±0.5^{0}C, concentration 1.85×10^{-4}m, particle size <55μm)

Table 3: Effect of pH on adsorption of Cd (II) by Rice husk ash (modified) at different pH.

Time (Min)	pH 5.5		pH 6.5		pH 7.5		pH 8.5	
	Amount adsorbed mg/g	Percentage of Adsorption	Amount adsorbed mg/g	Percentage of Adsorption	Amount adsorbed mg/g	Percentage of Adsorption	Amount adsorbed mg/g	Percentage of Adsorption
20	0.082	14.28	0.178	33.10	0.192	38.13	0.128	23.10
40	0.129	22.72	0.282	52.84	0.280	57.90	0.216	39.86
60	0.172	28.82	0.329	60.41	0.346	67.99	0.246	46.58
80	0.180	30.56	0.342	64.63	0.370	72.10	0.282	52.68
100	0.188	34.59	0.352	68.62	0.382	73.62	0.282	52.68
120	0.197	36.84	0.382	70.10	0.396	76.27	0.296	55.12
140	0.197	36.84	0.382	70.10	0.396	76.27	0.296	55.12

(Temp. 30.0±0.5^{0}C, concentration 1.85×10^{-4}m, particle size <55μm)

Table 4: Comparison of rate constants (k^1.min^{-1}) for Cd (II) adsorption onto raw and functionalized rice husk ash across different pH conditions

Adsorbate	Adsorbent	Concentration	Temperature	pH	Overall mass transfer coefficient k^1.min^{-1}	Rate constant k_1.min^{-1}	Rate constant of desorption k_2.min^{-1}
Cd (II)	Unmodified Rice Husk Ash	1.85×10^{-4}M	30.0±0.5ºC	5.5 6.5 7.5 8.5	0.027 0.031 0.033 0.029	0.0083 0.0211 0.0230 0.0158	0.0186 0.0102 0.0101 0.0132
Cd (II)	Modified Rice Husk Ash	1.85×10^{-4}M	30.0±0.5ºC	5.5 6.5 7.5 8.5	0.030 0.038 0.045 0.033	0.0180 0.0204 0.0346 0.0215	0.0192 0.0176 0.0105 0.0117

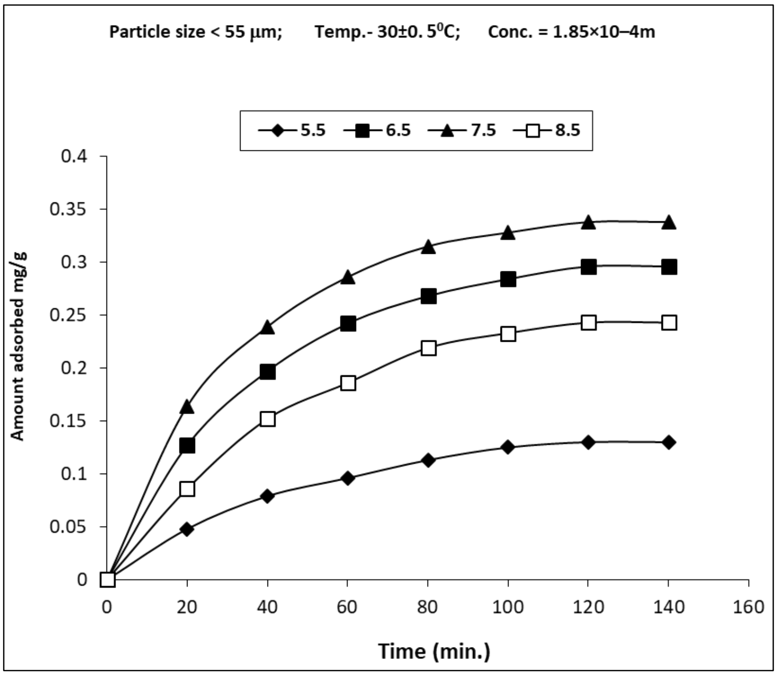

Fig 1: Effect of pH on adsorption of Cd(II) by Rice husk ash (unmodified) at different pH

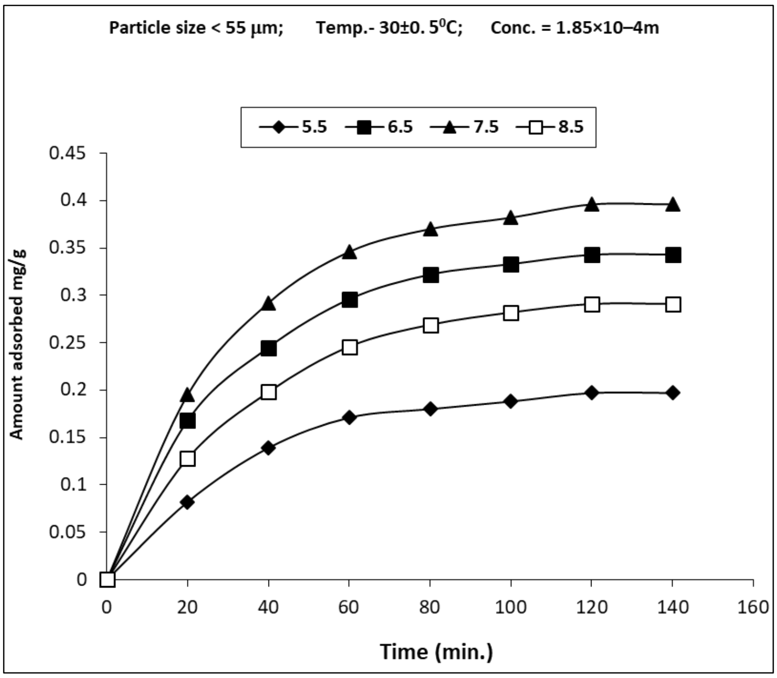

Fig 2: Effect of pH on adsorption of Cd(II) by Rice husk ash (modified) at different pH

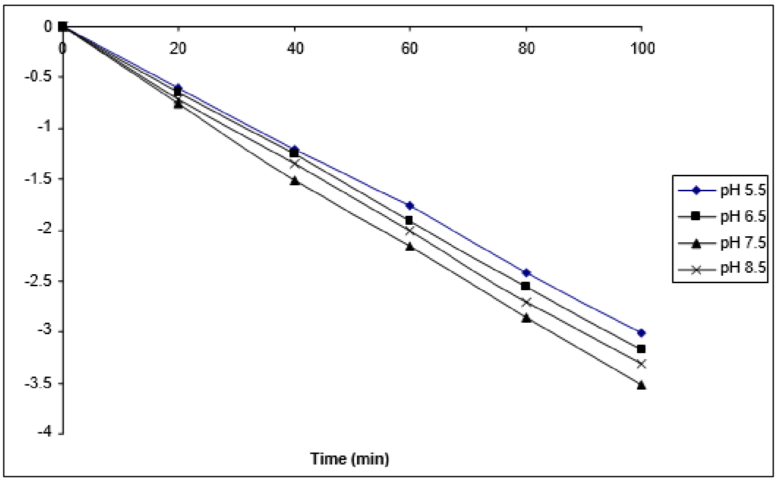

Fig 3: Linearized kinetic plots for the adsorption of Cd (II) on Rice husk ash (unmodified) at different pH.

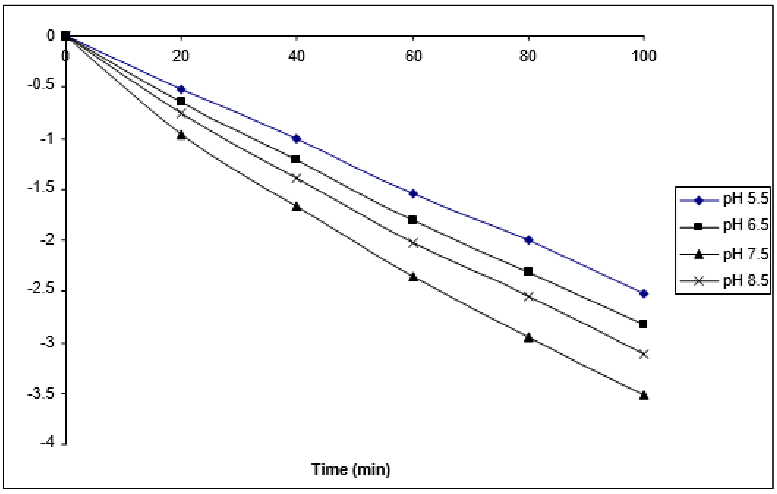

Fig 4: Linearized kinetic plots for the adsorption of Cd (II) on Rice husk ash (modified) at different pH.

Results and Interpretation

The removal efficiency of Cd (II) ions by eco-friendly, non-conventional Rice Husk Ash (RHA) is profoundly strongly governed by the initial pH value Experimental data indicate that removal efficiency is minimal under highly acidic conditions, rises significantly within the near-neutral range, and eventually plateaus or transitions into chemical precipitation at higher alkalinity. For modified RHA, the maximum adsorption capacity reached 0.396 mg/g (76.27% removal) at an optimal pH of 7.5, as shown in Table 2, 3 and Figure 1. In comparison, unmodified RHA exhibited a lower adsorption capacity of 0.338 mg/g (63.42% removal) at the same pH level, documented in Table 4 and Figure 2.

The kinetic studies, represented by the rate constants k_1 and k_2 in Figures 3 and 4, further confirm that the medium's pH directly dictates the adsorption rate for both modified and unmodified adsorbents. While higher pH levels facilitate cadmium removal from the aqueous phase, this is partially attributed to chemical sedimentation rather than the surface properties of the RHA alone- a phenomenon corroborated by previous research from Al-Degs *et al*. (2006), Anwar *et al*. (2010), Chen *et al*. (2011), Nurhasni *et al*. (2012), and Yadav *et al*. (2024).

Discussion of the Mechanisms of Adsorption

The pH of the adsorbent-adsorbate system acts as a decisive governing factor that dictates the rate, extent, and fundamental mechanism of the adsorption process. Current findings suggest that the sequestration of cadmium by Rice Husk Ash (RHA) is achieved through a synergistic combination of electrostatic attraction and surface complexation. The naturally porous and silica-rich architecture of the ash provides a high density of active sites; when these sites undergo deprotonation at higher pH levels, they transform into a powerful chemical filter for heavy metal ions. The robust stability and high efficiency observed at pH 7.5 confirm that RHA is a highly viable, sustainable, and low-cost solution for treating neutral-range industrial wastewater. By utilizing this agricultural byproduct, high-performance remediation is possible without the logistical burden or financial expense of traditional chemical additives.

Conclusion

The removal of Cd (II) utilizing rice husk ash (RHA) highlights the potential of non-conventional, agricultural byproducts as sustainable adsorbents. Through comparative analysis, it is evident that modified RHA serves as a significantly more effective medium than its unmodified counterpart. This enhanced performance is primarily stemming from the fact that both the rate and Adsorption magnitude are highly sensitive to fluctuations in solution pH and the surface morphology characteristics of the adsorbent. By chemically or thermally altering the ash, the density of active binding sites is optimized, allowing for superior metal sequestration across a broader range of conditions. Consequently, modified rice husk ash emerges as a more efficient, cost-effective, and robust a functionalized adsorbent for the mitigation of heavy metal contamination in aqueous systems environments. These kinetics were validated through the batch adsorption of Cd (II) unmodified and modified rice husk ash across various pH levels (5.5, 6.5, 7.5, and 8.5) and concentration ranges. The resulting linear plots confirmed that these systems consistently follow first-order reaction kinetics. Consequently, these findings offer a practical framework for developing wastewater treatment technologies, enabling the optimization of pollutant removal efficiency by adjusting system parameters such pH levels and initial concentration when using low-cost, non-conventional adsorbents.

The findings reveal that the adsorption process follows first-order reversible reaction kinetics, a conclusion supported by the linear plots of ln (1−u t) versus t. The Overall mass transfer coefficient (K') was determined from the slopes of these plots, allowing for the calculation of individual rate constants for adsorption (K_1) and desorption (K_2).

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