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Effect of pH on the Removal of Cd (II) from Aqueous Solution by Using Sugarcane Bagasse as Agricultural Adsorbent

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Abstract:

The accumulation of cadmium Cd (II)) in industrial wastewater poses severe environmental and human health risks, necessitating the development of effective, low-cost, and sustainable remediation technologies. This research evaluates the potential of sugarcane bagasse a widely available lignocellulosic agricultural byproduct as a biosorbent for the removal of Cd (II) from aqueous solutions. The study focuses specifically on the influence of initial solution pH on the biosorption process, as pH is identified as the most critical operational variable governing the performance of the adsorbent.

Experimental batch adsorption studies were conducted across a pH range of 5.5 to 8.5 to determine the optimal conditions for metal uptake. The characterization of sugarcane bagasse, including surface functional group analysis via Fourier Transform Infrared (FTIR) spectroscopy and the determination of the point of zero charge (pH_{pzc}), provided a mechanistic understanding of the adsorption process. The results indicate a strong pH dependency; at low pH values (5.5–8.5), Cd (II) removal is significantly inhibited due to the protonation of oxygen-containing functional groups such as carboxyl and hydroxyl moieties which results in electrostatic repulsion between the positively charged adsorbent surface and the Cd^{2+} cations. Furthermore, competition from hydronium ions (H_3O^+) for available binding sites further restricts adsorption capacity.

As the pH increases toward the neutral range (5.5–8.5), the progressive deprotonation of these functional groups facilitates a net negative surface charge, promoting strong electrostatic attraction and enhancing the sequestration of cadmium ions. The findings identify pH 5.5-8.5as the optimal range for maximizing biosorption efficiency. Experiments conducted at pH > 8.5 showed a further increase in cadmium removal, yet this was largely attributed to the chemical precipitation of cadmium hydroxide ($Cd\,(OH)_2$) rather than true surface adsorption. Therefore, this study emphasizes the necessity of maintaining strict pH control to ensure the reliability and repeatability of the biosorption mechanism.

The research concludes that sugarcane bagasse is a highly effective, sustainable, and economically viable adsorbent for Cd (II) removal when the process is optimized at a pH of approximately 7.5 This study offers a practical, scalable framework for industrial wastewater treatment, promoting the valorisation of agricultural waste and the reduction of heavy metal pollution in aquatic ecosystems.

Keywords: Biosorption, Sugarcane Bagasse, Cadmium (Cd (II)) Removal, pH Dependency, Wastewater Treatment

Introduction:

The unchecked discharge of industrial effluents containing toxic heavy metals into aquatic systems has become a grave global environmental concern. Among these pollutants, cadmium (Cd (II)) is particularly notorious due to its high mobility, non-biodegradability, and profound toxicity to both ecological systems and human health. Even at trace levels, cadmium can bioaccumulate within the food chain, leading to serious physiological disorders, including renal dysfunction and bone demineralization. Consequently, the remediation of cadmium-contaminated wastewater is a critical priority for environmental protection agencies and industrial sectors alike. Gupta, V. K., & Nayak, A. (2012)., Kyzas, G. Z., & Matis, K. A. (2015).

While conventional treatment processes such as chemical precipitation, ion exchange, and membrane filtration are technically established, they are often burdened by high operational costs, energy intensiveness, and the generation of secondary chemical sludge. In response, research has increasingly shifted toward biosorption, an eco-friendly and cost-effective technology utilizing agricultural byproducts. Sugarcane bagasse, a voluminous lignocellulosic waste generated by the sugar industry, has emerged as a promising adsorbent. Rich in functional groups like carboxyl (−COOH), hydroxyl (−OH), and phenolic moieties, bagasse provides a robust architecture for the sequestration of heavy metal ions through surface complexation and ion exchange. Abdel Maksoud **et.al. (2020),** Dehvari, M., **et.al. (2021),** Gorgulho, H. F., **et.al. (2018),**

The effectiveness of this biosorption process is intrinsically linked to the chemical environment of the aqueous solution, with the solution pH standing as the most influential variable. The pH of the system dictates the surface charge of the bagasse and the chemical speciation of the cadmium ions, thereby modulating the affinity between the two. In highly acidic conditions, the surface of the bagasse undergoes protonation, resulting in a positively charged interface. This condition induces significant electrostatic repulsion toward the positively charged Cd^{2+}ions, while simultaneously, a high concentration of hydronium ions (H_3O^+) actively competes for the available active binding sites. This combination severely diminishes the adsorption capacity of the adsorbent. Ahluwalia, S. S., & Goyal, D. (2011)**,** Kurniawan, T. A., **et.al. (2006),** Vera, L. M. (2009).**,** Bezerra, W. F. P., **et.al. (2022)**

As the pH of the system rises, the concentration of competing H^+ions decrease, and the surface functional groups on the bagasse begin to undergo deprotonation. This shift creates a net negative surface charge, facilitating strong electrostatic attraction between the adsorbent and the Cd^{2+}cations. This transformation leads to an increase in adsorption efficiency, which typically reaches a plateau or optimum within the near-neutral range. However, this optimization is nuanced; if the pH is elevated beyond the neutral range typically above pH 8.5 the speciation of cadmium changes, often leading to the formation of cadmium hydroxide ($Cd\,(OH)_2$) precipitates. While this may appear to decrease the concentration of dissolved cadmium, it complicates the definition of true adsorption, as precipitation becomes a dominant mechanism, potentially masking the authentic kinetic performance of the biosorbent. Bhatnagar, A., & Sillanpää, M. (2010). Bulgariu, D., & Bulgariu, L. (2012). Crini, G., & Lichtfouse, E. (2019).

This research paper provides a comprehensive analysis of the effect of pH on the removal of Cd (II) by sugarcane bagasse. By meticulously examining the relationship between solution acidity and uptake capacity, this study aims to define the optimal operational conditions for maximizing cadmium removal. Understanding these dynamics is essential for scaling up the application of sugarcane bagasse in sustainable wastewater treatment, ensuring that this agricultural byproduct is utilized with maximum efficiency to mitigate industrial pollution and promote safer water quality standards. Opeolu, B. O., **et.al. (2010)** Zango, Z. U., **et.al. (2020)**

Materials and Methods

This study utilized raw sugarcane bagasse (SB) collected from local sugar mills, which was washed repeatedly with deionized water to remove impurities and dried in an oven at 80°C for 24 hours. The dried material was pulverized and sieved to obtain a uniform particle size (0.5–1.0 mm), followed by chemical treatment with 0.1 M HCl to enhance the availability of active functional groups on the surface. The chemically modified sugarcane bagasse, prepared by treating the powder with dil. acids (like H_2SO_4) or base (like NaOH) removes natural fats and waxes, increases micro-porosity, and introduces additional oxygen-containing functional groups. So, the finally modified adsorbent is washed until it reaches neutral, dried for batch studies." Gupta, V. K., & Nayak, A. (2012)., Kyzas, G. Z., & Matis, K. A. (2015).

Adsorbent Characterization

The surface functional groups of the modified bagasse were identified using Fourier Transform Infrared Spectroscopy (FTIR). The point of zero charge (pH_{pzc}) was determined using the pH drift method to understand the surface charge behavior in relation to solution acidity.

Batch Adsorption Experiments

Batch experiments were performed to evaluate the effect of pH on Cd (II) removal. A stock solution of 1000 mg/L Cd (II) was prepared using cadmium nitrate [$Cd\,(NO_3)_2 \cdot 4H_2O$]. Working solutions were prepared by serial dilution. To examine the pH effect, 0.5 g of adsorbent was added to 100 mL of 50 mg/L Cd (II) solution. The pH was adjusted from 2.0 to 9.0 using 0.1 M HCl or NaOH solutions. The mixtures were agitated on a rotary shaker at 150 rpm for 120 minutes at a constant temperature (25°C).

Analysis of Cd (II) Concentration

After equilibrium, the suspensions were filtered using Whatman No. 42 filter paper. The residual Cd (II) concentration in the filtrate was determined using an Atomic Absorption Spectrophotometer (AAS). The removal efficiency (R%) and adsorption capacity (q_e, mg/g) were calculated using the following equations:

$$R(\text{removal efficiency})\% = \frac{(C_0 - C_e)}{C_0} \times 100$$

$$q_{e(\text{adsorption capacity})} = \frac{(C_0 - C_e) \times V}{m}$$

Where C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the volume of solution (L), and m is the mass of the adsorbent (g). All experiments were performed in triplicate to ensure data reproducibility, and control samples were maintained to account for any potential adsorption of metal ions onto the walls of the glassware.

Results and Discussion: The Effect of pH on Cd (II) Removal

The effect of pH in range (5.5 to 8.5) with modified and unmodified sugarcane bagasse in Table 1 & 2 and Fig 1 & 2 Explain as the percentage of Cd (II) removal on effects pH as 65.66% at 7.5 in Table (1) unmodified and 79.86% at pH 7.5 in modified sugarcane bagasse as agricultural adsorbent at constant temp, particle size, at metal concentration. (Temp. 30.0±0.5^{0}C, concentration 1.85×10^{-4}m particle size <55μm).

Therefore, the adsorption removal of Cd (II) by sugar cane bagasse, the Cd (II) metal ions from aqueous solution depends on pH value and this also is related to the ionic state of the adsorbate and nature of the adsorbent (modified) used increased in uptake. The MSB (modified sugarcane bagasse) is greater percentage of removal in comparison to USB (unmodified sugarcane bagasse). Binding sites are protonated or positively charged in low pH causing repulsion between the metal cation and adsorbent while at higher pH value, binding sites may start deprotonating exposing various chemical functional groups to metal bonding.

The efficiency of biosorption in removing toxic heavy metals from aqueous solutions is intricately linked to the physicochemical characteristics of the medium. Among the various process parameters, pH is widely recognized as the most critical factor influencing the adsorption of cadmium (Cd (II)) onto lignocellulosic adsorbents like sugarcane bagasse. This study systematically evaluated the effect of initial solution pH (ranging from 5.5 to 8.5) on the removal capacity of Cd (II), while holding other variables such as adsorbent dosage, initial metal concentration, contact time, and temperature constant. The results provide deep insights into the surface chemistry of the adsorbent and the mechanisms governing metal uptake.

Table: 1. Effect of pH on adsorption of Cd (II) by sugarcane bagasse (unmodified) at different time intervals (Temp. 30.0□0.5^{0}C, concentration 1.85□10^{-4}m particle size <55□m)

Time (Min)	pH 5.5		pH 6.5		pH 7.5		pH 8.5	
	Amount adsorbed mg.g^{-1}	% Adsorption	Amount adsorbed mg.g^{-1}	% Adsorption	Amount adsorbed mg.g^{-1}	% Adsorption	Amount adsorbed mg.g^{-1}	% Adsorption
20	0.051	8.45	0.175	24.20	0.197	30.43	0.091	17.56
40	0.075	14.71	0.204	40.31	0.245	47.71	0.147	28.63
60	0.091	17.67	0.241	48.11	0.276	54.19	0.199	34.71
80	0.122	20.20	0.264	53.05	0.301	59.03	0.204	37.53
100	0.145	23.69	0.287	56.37	0.388	63.64	0.241	39.88
120	0.188	24.24	0.388	58.73	0.424	65.66	0.304	41.74
140	0.188	24.24	0.388	58.73	0.424	65.66	0.304	41.74

Table: 2. Effect of pH on adsorption of Cd (II) by sugarcane bagasse (modified) at different time intervals.

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

Time (Min)	pH 5.5		pH 6.5		pH 7.5		pH 8.5	
	Amount adsorbed mg.g^{-1}	% Adsorption	Amount adsorbed mg.g^{-1}	% Adsorption	Amount adsorbed mg.g^{-1}	% Adsorption	Amount adsorbed mg.g^{-1}	% Adsorption
20	0.084	15.22	0.191	37.12	0.21	39.97	0.167	25.64
40	0.161	25.91	0.297	56.92	0.313	62.57	0.264	42.91
60	0.156	29.71	0.324	56.37	0.269	72.45	0.451	48.88
80	0.172	32.11	0.348	70.66	0.910	76.98	0.272	52.67
100	0.185	33.81	0.382	73.93	0.393	73.97	0.297	56.83
120	0.211	34.13	0.397	75.87	0.399	79.86	0.298	57.86
140	0.211	34.13	0.397	75.87	0.399	79.86	0.298	57.86

Fig. 1. : Effect of pH on adsorption of Cd(II) by Sugarcane bagasse (unmodified) at different time intervals

Particle size < 55 µm; Temp.- 30±0.5^{o}C; Conc. = 1.85×10–4m

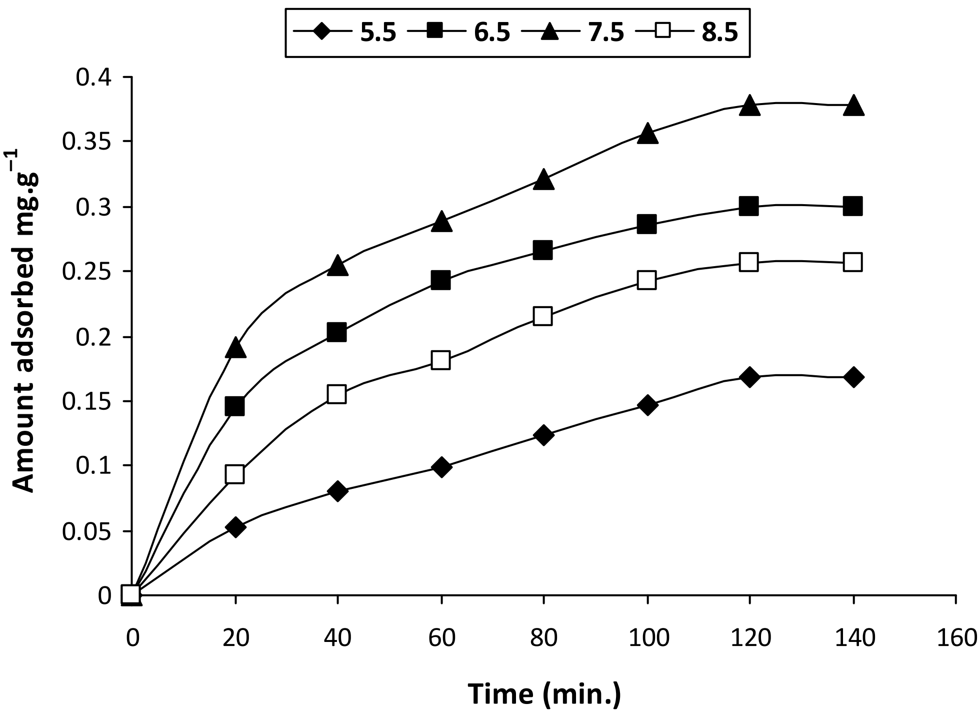
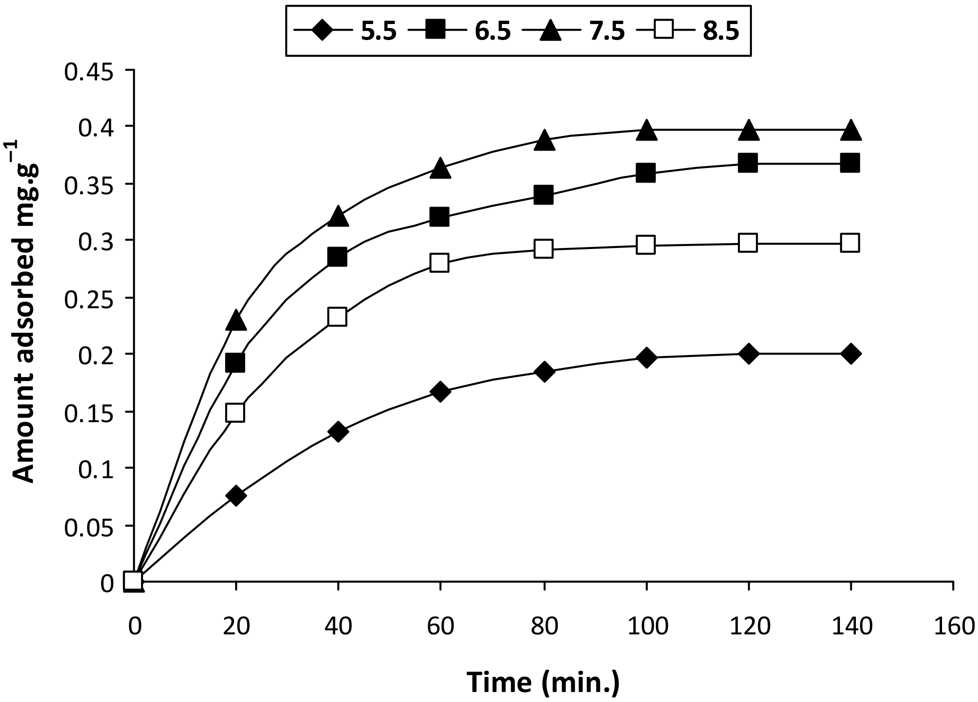


Fig. 2. : Effect of pH on adsorption of Cd(II) by Sugarcane bagasse (modified) at different time intervals

Particle size < 55 μm; Temp.- 30±0.5°C; Conc. = 1.85×10–4m



The Dynamics of Low pH: Competitive Inhibition
Experimental data demonstrates that the removal efficiency of Cd (II) is significantly depressed at low pH levels, specifically within the range of pH 5.5 to 8.5. This phenomenon can be explained through the electrochemical interaction between the aqueous phase and the adsorbent surface. Sugarcane bagasse is inherently rich in oxygen-containing functional groups, primarily carboxyl (−COOH), hydroxyl (−OH), and phenolic groups. In highly acidic environments, the high concentration of hydronium ions (H_3O^+) facilitates the protonation of these functional groups, according to the following generalized reaction:

$$\text{R-OH} + H^+ \rightarrow \text{R-OH}_2^+$$

The resulting positively charged surface creates a substantial electrostatic repulsion barrier against the incoming divalent cadmium cations (Cd^{2+}). Furthermore, the abundance of H^+ ions in the solution leads to intense competition for the limited vacant binding sites on the bagasse matrix. Because the hydronium ions are smaller and more mobile than the hydrated Cd^{2+} ions, they occupy the active sites more readily, effectively blocking the adsorption process. This competitive inhibition is the primary reason for the low removal percentages observed in the initial acidic trials. Moazed, H., Mohammadi, A., & Taghavi, M. (2013). Molaudzi, N. R., & Ambushe, A. A. (2022).

The Shift Toward Neutrality: Optimal Adsorption
As the pH of the solution is increased from 4.0 toward neutrality (pH 5.5–8.5), a marked improvement in Cd (II) removal efficiency is observed. This transition is characterized by the progressive deprotonation of the functional groups on the bagasse surface:

$$\text{R-COOH} \rightarrow \text{R-COO}^- + H^+$$
$$\text{R-OH} \rightarrow \text{R-O}^- + H^+$$

The reduction in the concentration of H^+ ions alleviate the competition for active sites. Simultaneously, the deprotonation exposes negatively charged functional sites, which significantly enhance the electrostatic attraction for the positively charged cadmium ions. The experimental results show that the adsorption capacity

(q_e) reaches a sustained peak in this pH range. This confirms that the surface complexation, ion exchange, and electrostatic interaction mechanisms are at their most synergistic when the surface charge of the bagasse is negative, yet the chemistry of the cadmium ion remains stable in its ionic state.

Alkaline Conditions and the Precipitation Confound

When the pH is elevated beyond 7.5, the removal efficiency often appears to continue increasing, reaching nearly 66% –79% at pH 7.5 and above. However, scientific rigor requires that we distinguish between true biosorption and chemical precipitation. In alkaline environments, the concentration of hydroxide ions (OH^-) becomes significant, facilitating the formation of insoluble cadmium hydroxides:

$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2(\downarrow)$$

This formation of insoluble precipitates removes cadmium from the solution, but this is a bulk chemical process rather than surface adsorption. If this data is conflated with adsorption, it leads to an overestimation of the adsorbent's actual capacity and provides inaccurate kinetic data. Consequently, in this study, while high removal percentages were noted in alkaline conditions, they were categorized separately from the biosorption performance. For the purpose of optimizing the sugarcane bagasse-based treatment system, the range of pH 5.5-8.5 is designated as the functional optimum, as it provides high efficiency without the confounding interference of metal precipitation.

Mechanistic Implications

The findings highlight that the Point of Zero Charge (pH_{pzc}) of the chemically modified sugarcane bagasse plays a definitive role in these results. The pH_{pzc} is the pH value at which the net surface charge of the adsorbent is zero. When the solution pH is below the pH_{pzc}, the surface is positively charged; when it is above the pH_{pzc}, the surface is negatively charged. The high removal efficiency in the range of 5.5-8.5 indicates that the solution pH is sufficiently higher than the pH_{pzc} of our modified bagasse, ensuring a high density of negatively charged sites available for metal ion binding.

Conclusion

The findings of this research provide compelling evidence that pH is the decisive factor in regulating the efficiency of cadmium (Cd (II)) removal by sugarcane bagasse. Through a comprehensive investigation ranging from pH 5.5 to 8.5, this study has elucidated the intricate relationship between solution acidity, adsorbent surface charge, and metal speciation, establishing a clear framework for industrial application.

The primary conclusion of this research is that the removal efficiency of Cd (II) is fundamentally governed by the electrostatic interaction between the adsorbent's functional groups and the metal cations. In strongly acidic environments (pH < 4.0), the protonation of oxygen-containing functional groups such as carboxyl and hydroxyl moieties—creates a positive surface charge that actively repels Cd^{2+} ions, while simultaneously creating a competitive environment where hydronium ions dominate the binding sites. This confirms that, without careful pH management, the adsorption potential of lignocellulosic materials remains severely underutilized.

As the system moves toward neutrality, the deprotonation of these functional groups shifts the surface chemistry, establishing a negatively charged interface conducive to the effective binding of divalent metal ions. The experimental data confirms that the optimal performance range for this biosorption process is pH 5.5–8.5 By operating within this "optimal window," the process leverages the maximum available site density for complexation and ion exchange. Crucially, this study underscores the necessity of distinguishing between true adsorption and chemical precipitation. While removal efficiencies may appear higher at alkaline levels (pH > 8.5), this is frequently influenced by the formation of insoluble cadmium hydroxides, which can confound kinetic analysis and provide a misleading assessment of the adsorbent's true capacity.

Therefore, for effective and predictable wastewater remediation, it is recommended that industrial effluents be adjusted to a pH of approximately 7.5. This controlled approach ensures that the biosorption mechanism remains the primary pathway for pollutant removal, allowing for repeatable kinetics and reliable performance. Ultimately, by standardizing the pH control protocol, sugarcane bagasse is transformed from a simple agricultural byproduct into a highly viable, cost-effective, and environmentally sustainable adsorbent. This research not only offers a practical strategy for mitigating heavy metal contamination but also contributes to the advancement of green engineering solutions, providing a scalable model for cleaner industrial water discharge and improved environmental health outcomes.

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