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Batch Investigations on Cadmium Ion Adsorption Using Activated Carbon with a Focus on pH, Adsorbent Dosage, and Contact Time

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ABSTRACT

One of the most significant environmental issues at the moment is wastewater contaminated with heavy metals. Considering how persistent they are, heavy metal removal from the environment is very important. Adsorption techniques are being used by many researchers to remove heavy metals and one common adsorbent used in these procedures is activated carbon. The aim of this research has been to utilise activated carbon in batch investigations to remove Cadmium (Cd) ions. Several experimental conditions have been considered to see the effect of pH, adsorbent dosage, and contact time. The pH and the adsorbent dose has been varied to find out the optimum pH and the optimum adsorbent dose. The Cd solutions has been prepared with varying concentrations at an optimum pH value for each solution. The initial and final absorbance has been noted before and after adding the optimum dose of activated carbon to each solution to study the effect of contact time and percentage removal efficiency of Cd. Maximum removal efficiency of 88.01% has been observed for Cd at a contact time of 60 minutes. The adsorption results has been validated by isotherm study and the Freundlich model gave a coefficient of regression (R^2) value of 0.9504. Maximum Cd ions removal efficiency at the optimum pH and optimum dosage of activated carbon has been found to be 86.81% and 89.65%, respectively. According to the study's findings, activated carbon works well as an adsorbent when it comes to removing Cd.

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INTRODUCTION

In the current global context, heavy metal pollution poses a serious threat to the ecosystem and has reduced freshwater availability for the growing population. Because of their toxicity, persistence, and capacity for bioaccumulation, heavy metals are not biodegradable and can have detrimental effects on the trophic level (Genchi *et al*., 2020). Heavy metal compounds are widely used in steel fabrication, paint and pigment, wood preservative, cement, electroplating, and metal processing sectors. Numerous chemical and physical techniques, like ion exchange, ultrafiltration, precipitation, and reverse osmosis, can be used to extract these metals from wastewater (Salmani *et al*., 2013; Sudha & Celine, 2008; Ullah & Haque, 2011). The world's nations are facing grave challenges because of the deteriorating quality of their water. Numerous illnesses could result from wastewater with high levels of cadmium (Cd). Humans are vulnerable to exposure to this extremely dangerous metal in their homes or places of employment, even at very low concentrations (0.5 mg/l). Cd and its derivatives are considered carcinogenic by the International Agency for Research on Cancer (IARC, 2022). Cd ingestion and inhalation

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can result in kidney failure, serious lung damage, and even death from long-term exposure. Oxidative stress and nutritional deficits may result from excessive Cd concentrations in the soil. In 2014 the successful removal of Cd (II) from aqueous mixture using activated carbon was explored by Chaudhary *et al*., because heavy metals are of critical concern in industrialized countries (Chaudhary *et al*., 2014). Naiya et.al. in 2008 characterized the clarified sludge, a major waste product generated in the steelmaking process, and assess its suitability for removing Cd (II) from aqueous mixture (Naiya *et al*., 2008).

Kumar et.al. in 2012 removed Cd (II) from aqueous mixture by using cashew nutshell (CNS) as an affordable adsorbent (P. S. Kumar *et al*., 2012). Minceva et. al. in 2008 studied the performance of natural zeolite tuff in removing Cd^{2+}, Pb^{2+}, and Zn^{2+} from aqueous mixture and compare it to the performance of commercial granulated activated carbon (Minceva *et al*., 2008). Abuilaiwi in 2020 studied that the polyamidoxime resin demonstrated a higher adsorption capability for Cd (II), Cr (III), and Pb (II) (Abuilaiwi, 2020). Rao et.al.in 2010 studied the use of adsorbents made from industrial and agricultural waste materials, as well as low-cost synthetic oxides, for the purpose of Cd removal (Rao *et al*., 2011). Xu. et.al. in 2014 studied the effectiveness of the new substance as an adsorbent (made from waste PCBs) for removing Cd ions (Xu *et al*., 2014). Zhai *et al*. in 2004 studied the efficacy of an adsorbent made from sewage sludge for the removal of Cd and Ni ions from water (Zhai *et al*., 2004). Yangisawa et.al. in 2010 investigated the preparation of a composite material that combines magnesium with activated carbon derived from coconut shells for removing the Cd and Zn ion (Yanagisawa *et al*., 2010). Singanan in 2011 studied the effective removal of Pb (II) and Cd (II) from aqueous mixtures, with a focus on industrial wastewater treatment (Singanan, 2011). Kumar & pawan in 2019 studied the appropriateness of sludge from the gas industry as an adsorbent to remove Cd ions (P. Kumar & Kumar, 2019). In 2022, Saeed *et al*. looked at how well rice husk biochar worked as an adsorbent to remove Cd (II) ions from a solution (Ameen Hezam Saeed *et al*., 2022).

In 2014, Kavand *et al*. investigated the best way to use commercial activated carbon to remove Cd (II), Ni (II), and Pb (II) from aqueous solutions (Kavand *et al*., 2014). Gran *et al*. in 2021 economically removed the heavy metals specifically cadmium (Cd) and chromium (Cr), from aqueous solution (Gran *et al*., 2021). The biosorption of cadmium ions on fish scales (FS) made from Sardina pilchardus was studied by Jaafar *et al*. in 2021 (Jaafar *et al*., 2021). In 2020, Molina *et al*. used three distinct adsorbents to assess the adsorption capability of metal ions, specifically Cd (II), Cr (VI), and Ni (II), from aqueous solution (Molina-Campos *et al*., 2020). Adebayo *et al*. in 2015 studied activated carbon derived from Vitellaria paradoxa (shea nut) shells, prepared using ortho-phosphoric acid, for the removal of Cd (II) ion (Adebayo *et al*., 2015). Huang *et al*. in 2018 evaluated the removal efficiencies of Bacillus cereus RC-1 for removing Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} (Huang *et al*., 2018). Villabona-ort, *et al*. in 2021 investigated the mechanisms of cadmium (Cd^{2+}) adsorption on residual biomasses derived from yam husks (Villabona-ort *et al*., 2021). Manjuladevi *et al*. in 2017 investigated the potential of activated carbon derived from Cucumis Melopeel (CM) as an adsorbent for the removal of Cr^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+} ions (Devi M, 2017). In 2019, Saini *et al* studied the removal of Cd(II) by modifying Dendrocalamus strictus charcoal powder (Saini *et al*., 2019).

These days, removing heavy metals from wastewater is essential, and it needs to be thoroughly studied. In the present study, commercially available activated carbon has been used as an adsorbent. The objective of this study has been to find the optimum pH, optimum activated carbon dose and how much contact time affects the amount of Cd ions removed from wastewater. In future other adsorbents like biosorbents or self-prepared variants of activated carbon can be explored as an adsorbent.

MATERIAL AND METHODS

Preparation of Stock Cadmium Solution

Cadmium Nitrate Tetrahydrate salt ($Cd(NO_3)_2.4H_2O$) of analytical grade has been used. 137 milligrams Cadmium Nitrate Tetrahydrate salt has been weighed on a clean and dry watch glass and then added to double distilled water (100 mL) in an A-grade volumetric flask and shaken well. Stock cadmium solution with concentration of 500 mg/l has been made according to Standard Method 3110 (APHA, 2017).

Preparation of Alizarin Red S or Indicator Solution

126.57 milligrams of Alizarin Red S (1, 2-dihydroxyanthraqui-none-3-sulphonic acid, sodium salt) powder has been weighed in a clean and dry watch glass and then added to 250 mL of double distilled water in an A-grade volumetric flask. The solution has been stored in an amber colored reagent bottle and prepared on a weekly basis.

Preparation of Standard Cadmium Solution

Standard solutions of 1 mg/l to 5 mg/l of Cd has been prepared using the stock cadmium solution in accordance with the dilution factor law. Calibration standards of 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5.0 mg/l of cadmium solutions has been prepared by adding 0.5 ml of Sulfuric acid (H_2SO_4) to each beaker. Then 50ml solution of each concentration has been transferred to 50 mL volumetric flasks and then 1 mL of Alizarin Red S has been added making the final volume equal to 51 mL, followed by shaking. The pH of all the calibration standards has been checked and found to lie between 1.5 and 2, as per Indian Standard code (IS:3186, 2006). Color of different intensities has been observed visually in the standards, and then absorbance has been evaluated by spectrophotometric analysis.

Adsorbent Used

Commercially available activated charcoal obtained from Chemigens Private Limited has been used as an adsorbent in this study. The batch investigation was conducted using certain weights of activated carbon, namely 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 grams, as adsorbent doses.

Metal Detection Instrumentation

The apparatus employed in the detection and determination of Cd metal in this study is UV-Visible Spectrophotometer (Hitachi U3900) with a quartz cell of 1cm and the measurements has been taken at a wavelength equal to 422 nm.

RESULTS AND DISCUSSION

The process of preparation of synthetic wastewater and its characterization has been explained in the following sections. Under a range of experimental settings, the effects of pH, adsorbent dosage, and contact time on the percent removal efficiency of cadmium ion have been studied. The results obtained are discussed below.

Effect of pH

Different solutions having cadmium concentration of 2 mg/l has been prepared with varying pH values from 1 to 10. Before adding 0.2 g/l of activated carbon to each solution the initial absorbance has been noted and after adding activated carbon the final absorbance has been evaluated after 24 hours by spectrophotometer, similar conditions have also been reported in (Ullah & Haque, 2011). Maximum cadmium removal efficiency of 86.81% has been observed at a pH value of 6 and a minimum percentage removal efficiency of 75.73% has been observed at a pH = 1. Therefore, the optimum pH is 6 for the maximum removal of cadmium. The graph in Figure 1 illustrates the association between the percentage removal efficiency of cadmium versus the pH value of the synthetic wastewater with adsorbent dosage of 0.2 g/l.

Effect of Adsorbent Dose

Now the dosage of activated carbon has been extensively studied by varying it from 0.2 to 1.2 grams per liter in the solutions having Cd concentration of 2 mg/l and optimum pH value of 6. Before adding the activated carbon, the initial absorbance has been noted and after adding 0.2 to 1.2 gm/l of activated carbon to each solution the final absorbance has been evaluated after 24 hours by spectrophotometer. The graph in Figure 2 illustrates the relationship between the percentage removal efficiency of cadmium versus the varying dosage of activated carbon at an optimum pH value of 6. An increasing trend in the removal efficiency of cadmium ion has been observed with an increase in activated carbon dose from 0.2 to 0.6 g/l. Maximum cadmium removal efficiency of 89.65% has been observed at an activated carbon dose of 0.6 g/l and a minimum percentage removal efficiency of 13.79% has been observed at an activated carbon dose of 1.2 g/l. Therefore, the optimum activated carbon dose value is 0.6 g/l for the maximum removal of cadmium.

Effect of Contact Time

The removal of cadmium has been studied as a function of contact time, with varying concentrations from 1 mg/l to 5 mg/l having an optimum pH = 6 for each solution. The initial absorbance has been noted prior to the addition of the optimum dose of activated carbon. Following the addition of the optimum dose of activated carbon (0.6 g/l) to each solution, the effect of increase in contact time over has been studied and the absorbance has been noted at an interval of 15 minutes upto 3 hours by spectrophotometer. The graph in Figure 3 illustrates the relationship between the percentage removal efficiency of cadmium versus the contact time at an optimum pH (6) and optimum activated carbon dose (0.6 g/l). At an optimum pH and optimum activated carbon dose, the maximum cadmium removal efficiency of different cadmium concentrations i.e., for 1.0 mg/l is 67% at 120 minutes, for 1.5 mg/l is 71% at 60 minutes, for 2.0 mg/l is 88% at 60 minutes, for 2.5 mg/l is 72.25% at 60 minutes, for 3.0 mg/l is 86.78% at 30 minutes, for 3.5 mg/l is 66% at 60 minutes, for 4.0 mg/l is 71% at 60 minutes, for

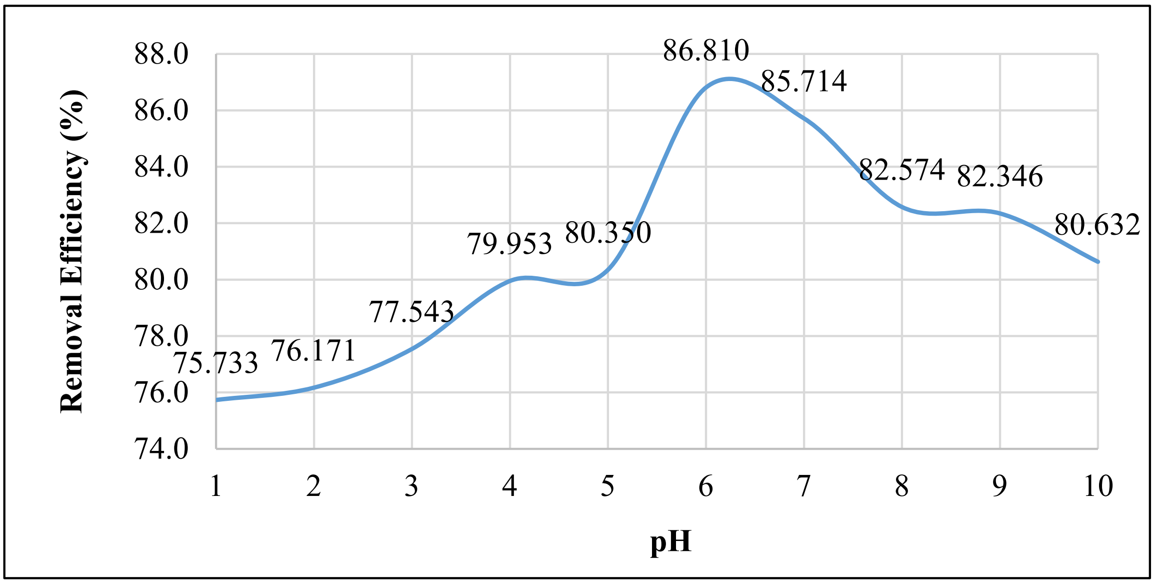

Fig. 1. Percentage removal efficiency of Cadmium vs pH with 0.2g/l of adsorbent dosage

4.5 mg/l is 70% at 15 minutes and for 5.0 mg/l 64% at 10 minutes with respect to contact time.

Comparison between Cd removal efficiency measured in the present study and other previously done studies are summarized in Table 1. While most of the prior research focused on the removal of Cd at higher concentrations using various adsorbents, our study specifically targets the removal of Cd at lower concentrations (1-5 mg/l) from wastewater. This distinction is significant because removing contaminants at lower concentrations often requires different strategies and can present unique challenges compared to dealing with higher levels of contamination. The results obtained in this study indicate that the maximum removal efficiency of Cd at optimum pH, optimum dosage and optimum contact time was found to be 86.81%, 89.65% and 88.01% respectively.

Validation Standard Adsorption Isotherms

When defining the solutes' adsorption behavior on certain adsorbents, the adsorption isotherms play a crucial role. The adsorption data obtained experimentally has been analysed using two adsorption isotherm methods i.e., Langmuir adsorption isotherm and the Freundlich adsorption isotherm at varied conditions of cadmium concentration.

The Langmuir isotherm operates under the presumption that sorption takes place at particular homogenous sites in the adsorbent (Langmuir, 1918).

An extended version of the Langmuir formula is:

$$q_e = \frac{q_0 b C_e}{1 + b C_e}$$

Concentration in the solution can be expressed in the linear form of the isotherm equation as:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0}$$

where,

q_0 = Maximum metal uptake in relation to the adsorbent's saturation capacity

b = Adsorption energy

q_e = Equilibrium amount of metal adsorbed on the activated carbon

C_e = Equilibrium concentration of metals ions

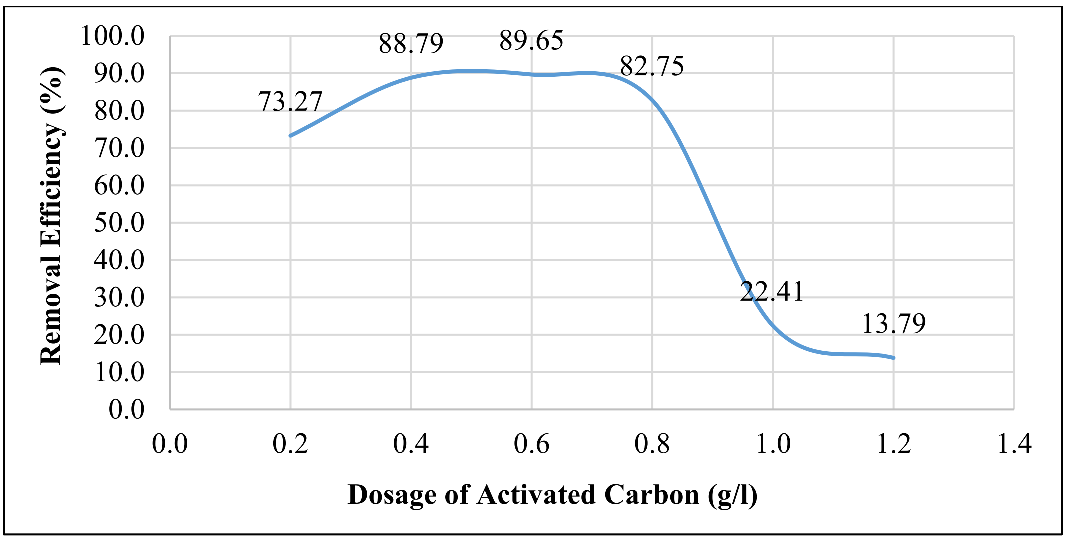

Fig. 2. Percentage removal efficiency of Cadmium vs dosage of activated carbon at pH = 6

Table 1. Cd adsorption efficiency comparison by different adsorbent

Adsorbent Used	Adsorbate (Cd Conc.)	Optimum Conditions	Adsorption Efficiency	References
Pistachio, Peanut, and Almond Shell	5 to 100 mg/l	pH = 6 adsorbent dosage = 0.25 to 0.8 g/l contact time = 45 minutes	52% - 84%	(Kayranli, 2022)
Magnetic Carbon Aerogel	20 to 100 mg/l	pH = 7 adsorbent dosage = 0.4 g/l contact time = 30 minutes	85% - 98.7%	(Li *et al.,* 2021)
Titanium Dioxide Nano particles (TiO_2, NPs)	30 mg/l	pH = 4.3 adsorbent dosage = 0.7 g/l contact time = 120 minutes	89.45%	(Irshad *et al.,* 2019)
Coconut Shell, Walnut Shell, Almond Shell	5 to 52 mg/l	pH = 6.5 adsorbent dosage = 15 g/l contact time = 150 minutes	83.7% - 100%	(Ayub *et al.,* 2019)
Cucumis Melo Peel	250 mg/l	pH = 6 adsorbent dosage = 0.25 g/l contact time = 180 minutes	97.95%	(Manjuladevi *et al.,* 2018)
Root Biomass of Water Hyacinth (Eichhornia Crassipes)	10 to 600 mg/l	pH = 6 adsorbent dosage = 0.2 g/100ml contact time = 150 minutes	63% - 86%	(Murithi *et al.,* 2014)
Commercial Activated Carbon	10 to 50 mg/l	pH = 6 adsorbent dosage = 6 g/l contact time = 120 minutes	100%	(Hydari *et al.,* 2012)
Wheat Stems	0.1 to 1.2 mmol/l	pH = 5 adsorbent dosage = 0.2 g/l contact time = 20 minutes	95%	(Tan & Xiao, 2009)
Olive Stone	15 to 45 mg/l	pH = 9 adsorbent dosage = 1.0 g/50ml contact time = 60 minutes	95%	(Kula *et al.,* 2008)
Commercial Activated Carbon	1 to 5 mg/l	pH = 6 adsorbent dosage = 0.6 g/l contact time = 45 minutes	86.81% - 89.65%	This Study

In the dimensionless version of the Langmuir isotherm, the expression of the separation factor (RL) is:

$$RL = \frac{1}{1 + bC_0}$$

where,
C_0 = Initial concentration of cadmium ion
b = Langmuir constant

The characteristics of the separation factor (RL) give us an idea whether the isotherm is, favourable, irreversible, linear, unfavourable. For favourable condition the RL should lie between zero and one, for irreversible condition RL is zero, for linear condition RL is equal to 1, and for unfavourable condition RL is greater than 1. It is generally known that the RL, which indicates the favourable adsorption condition, is less than 1 in all of the chosen concentrations of Cd ion.

An empirical equation based on a heterogeneous surface is given by the Freundlich expression as (Freundlich, 1906):

$$q_e = K_f C_e^{\ 1/n}$$

The linear form of this equation is:

$$log q_e = log K_f + \frac{1}{n} log C_e$$

where,
$logK_f$ = Measure of the adsorption capacity intercept
1/n = Adsorption intensity slope
Plots based on the Freundlich and Langmuir adsorption isotherms are shown in Figures 4

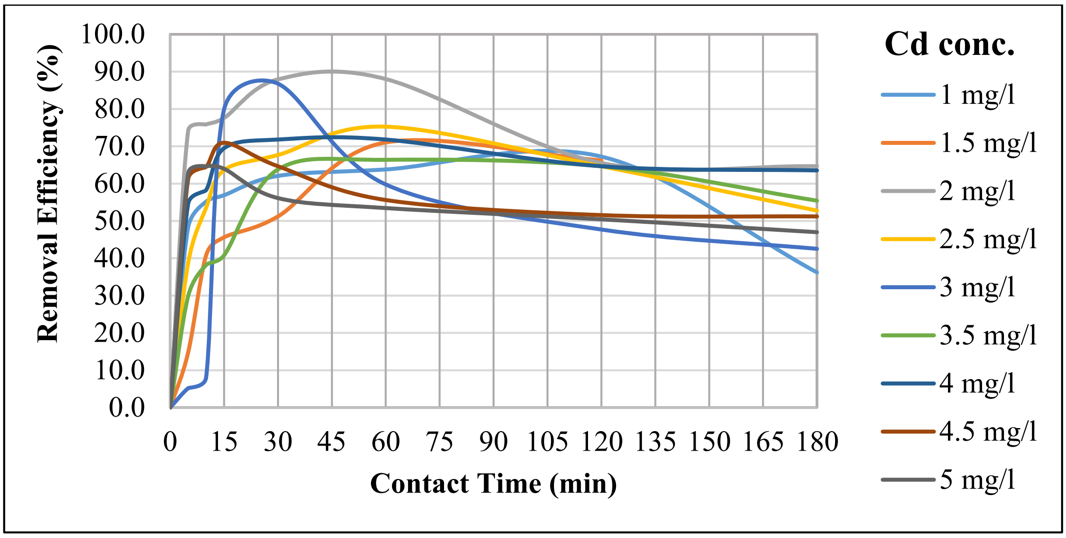

Fig. 3. Percentage removal efficiency of Cadmium vs contact time at an optimum dose of activated carbon and pH

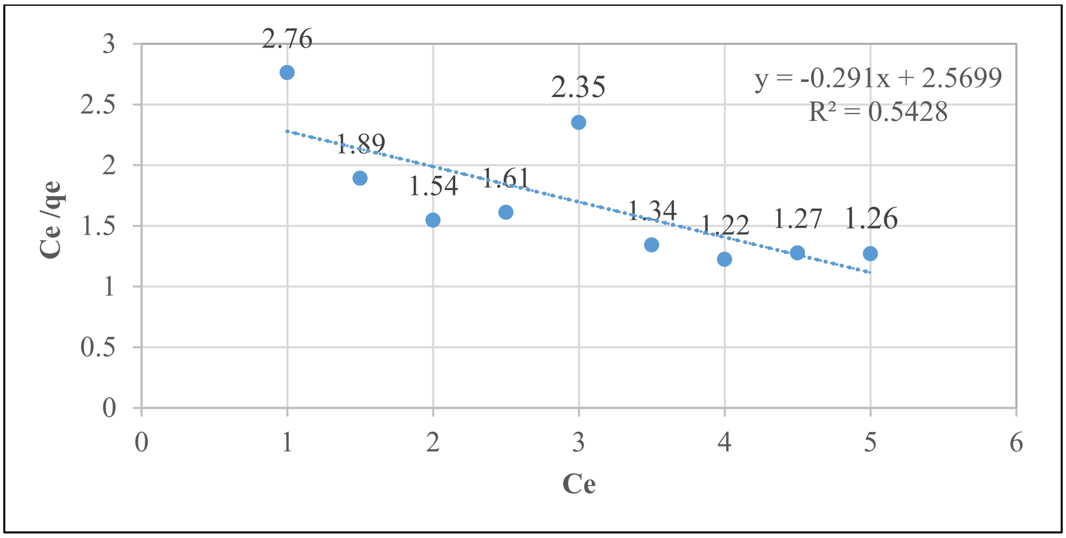

Fig. 4. Langmuir Adsorption Isotherm

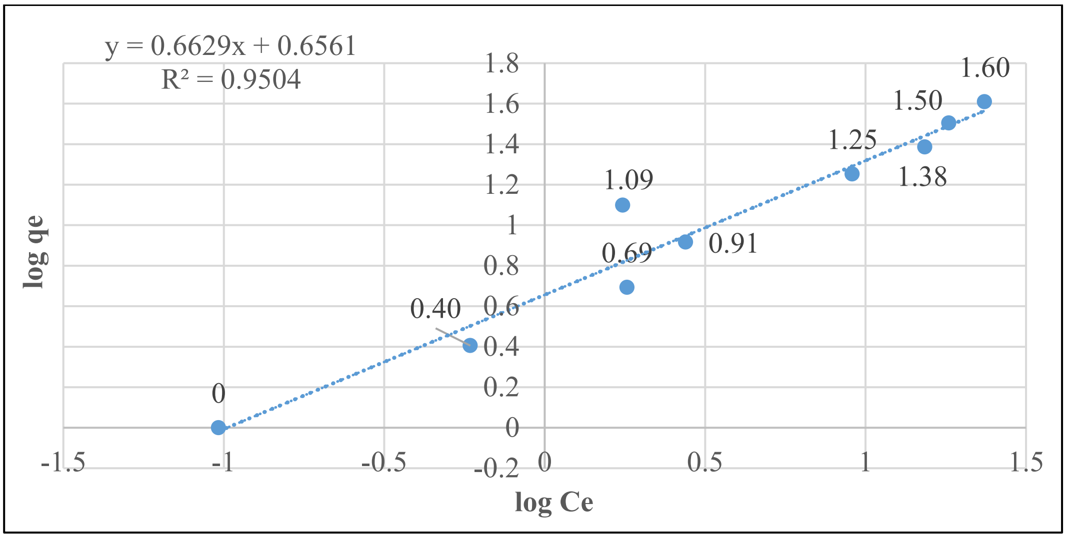

Fig. 5. Freundlich Adsorption Isotherm

and 5, respectively. From the graphs Freundlich isotherm model has been selected as the best fit model based on the coefficient of regression (R^2) value as 0.9504 when compared to Langmuir adsorption isotherm R^2 value as 0.5428.

CONCLUSION

This study addresses the removal of cadmium ion from wastewater by employing adsorption techniques using activated carbon as an adsorbent. The persistence of heavy metals in the environment necessitates effective removal techniques, and adsorption has proven to be a viable method. By conducting batch investigations, we explored the impact of various experimental conditions, including pH, adsorbent dosage, and contact time, to optimize the removal efficiency of Cd. Our findings indicate that the maximum removal efficiency of 88.01% for Cd was achieved at a contact time of 60 minutes. Additionally, the optimum conditions for pH and adsorbent dosage resulted in removal efficiencies of 86.81% and 89.65%, respectively. These results were further validated through isotherm studies, with the Freundlich model showing a high coefficient of regression (R^2) value of 0.9504, confirming the efficacy of activated carbon as an adsorbent for Cd ions. In conclusion, activated carbon has demonstrated significant potential in removing Cd from wastewater, with high efficiency under optimal conditions. This research underscores the importance of optimizing parameters such as pH, adsorbent dosage, and contact time to enhance the adsorption process. Future research should focus on scaling up this approach and exploring its applicability to other heavy metals and complex wastewater matrices. The successful application of activated carbon in this study provides a promising foundation for further advancements in wastewater treatment technologies.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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