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Kinetics of Cadmium Removal from Aqueous Solutions by Iron-enriched Biochar

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CADMIUM (Cd) is one of the most toxic elements in the environment. Its hazards are widely reported in many areas around the world, especially in Asia. Probably, contaminated water is the main routes of Cd toxicity to the living organisms. Thus, the current study investigates the efficiency of using biochar enriched with Fe for removal of Cd from artificially contaminated water and its kinetics. Accordingly, sugarcane bagasse was collected from the nearby juice bars and used for preparation of biochar. Afterwards, this product was submersed in ammonium ferrous sulphate solution (1000 mg L^{-1}) for 5 h and washed thoroughly with distilled water to removed unreacted Fe^{2+}. Subsequently, a batch technique was followed under lab conditions to find out the feasibility of using this type of biochar for removal of Cd from artificially contaminated water (56.5 mg Cd L^{-1}) within short time periods of contact extended to 360 min. A rapid initial increase occurred in sorbed Cd on surfaces of biochar enriched with Fe within the first 60 min of application; thereafter Cd sorption remained apparently constant. This sorption followed the power function model and the removal efficiency of Cd in this case did not exceed 46% of soluble Cd concentrations. In conclusion, biochar enriched with Fe might not be enough solely to attain successful removal of Cd from wastewaters.

Keywords: Cadmium; contaminated water; Fe enriched biochar; kinetic models; removal efficiency.

1. Introduction

Cadmium (Cd) is one of the most toxic elements in the environment, which has no known physiological role in living organisms (Hayat *et al.*, 2019). It is highly mobile and exhibits higher bioavailability than other toxic elements (Raj and Maiti, 2020). This, in turn, causes serious health problems (Yang *et al.*, 2022), e.g. interfere with genes (Đukić-Ćosić *et al.*, 2020), inhibit DNA repair mechanism, formation of ROS and the induction of apoptosis (Rani *et al.*, 2014).Its toxicity is widely reported in many areas around the world, e.g. Thailand and China (Yang *et al.*, 2022). People thereon suffer from renal tubular disease, osteomalacia, and Itai-itai disease (Yang *et al.*, 2022). This contaminant may also affect human reproduction and fertility (Kumar and Sharma, 2019). The main routes of Cd toxicity are through inhalation, food and water (Zhao *et al.*, 2023). In this study, we focus on Cd contamination in water and how to lessen its contamination level using efficient and cheap material, named biochar.

Many techniques (precipitation, flocculation, ion exchange, and membrane filtration) are applicable for removal of Cd from wastewater; yet they are almost costly and ineffective (Halttunen *et al.*, 2007). Alternatively, low-costs adsorbents are promising techniques (Pyrzynska, 2019). For example, biochar exhibits high adsorption capability for potentially toxic elements, including Cd (Zhang *et al.*, 2023). This product is the outcome of pyrolysis of organic residues under limited oxygen conditions (Bassouny and Abbas, 2019; Tolba *et al.*, 2021; Farid *et al.*, 2022; Khalil *et al.*, 2023; Mohamed *et al.*, 2024). Biochar exhibits a large surface area and a porous structure (Abdelhafez *et al.*, 2014; Abdelhafez *et al.*, 2021) which increase its capability to remove

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massive concentrations of this contaminant from wastewater (Chen *et al.*, 2020; Hamzenejad Taghlidabad *et al.*, 2020; Puglla *et al.*, 2020). Its efficiency can be upgraded when enriching it with Fe (Dad *et al.*, 2021).

In this case, iron compounds takes part in Cd adsorption and precipitation (Yuan *et al.*, 2020; Islam *et al.*, 2021). Thus, the current study investigates kinetics and efficiency of using biochar enriched with Fe for removal of Cd from wastewater within short time periods of contact extended to 360 min. We believe that the results of this study could improve our knowledge about the possible additives that can be used for efficient removal of Cd from wastewaters

2. Materials and Methods

2.1. Feedstock collection and preparation of biochar enriched with Fe

Sugarcane bagasse was collected from the nearby juice bars, washed with tap water, then distilled water and oven dried at 70 ^oC for 2 days. Afterwards, the dried material was crushed via pulverizer, then subjected to pyrolyses at 500 ^oC in a furnace for 2 h in the presence of N_2 gas, at a flow rate of 60 mL min^{-1}. The product was cooled at room temperature, finely ground to pass through a 1 mm sieve, then, submersed in ammonium ferrous sulphate solution (1000 mg L^{-1}) while being stirred with a magnetic stirrer at 40 ◦C for 5 h, filtered, washed with distilled water to remove the unreacted Fe^{2+}, and dried in a dryer at 60 ◦C. This product was acidic (pH=6.46, determined in 1:10 extract), and its contents of C, H, N, O and Fe were 74.94, 4.01, 9.92, 9.66 and 1.5%, respectively

1.2. Preparation of water artificially contaminated with Cd

An artificial contaminated water with Cd was prepared in the laboratory scale by dissolving cadmium nitrate tetrahydrate salt (Sigma Aldrich, ≥99%) in double distilled water (ddH_2O) to get 56.5mg Cd(II)L^{-1}.

2.3. The batch experiment

Thirty nine centrifuge cups were filled with 500 mL of the Cd contaminated water sample, then 0.25 g of Fe enriched biochar was added. Agitation was carried out continuously for 360 min. During this period, 3 cups were taken at the following time periods: 0, 30, 60, 90, 120, 150, 180, 210. 240. 270, 300, 330 and 360 min, centrifuged (SC-3610, Changzhou, China) at 3000 rpm for 10 min, filtrated using Whatman filter paper no 42 and C_e was determined in supernatants using Inductively Coupled Plasma *(ICP-OES Perkin Elmer 5300 DV*).

2.4. Data analyses and processing

Figures were plotted via Sigma plot 10. Cadmium sorption capacity qe (mg g^{-1}) and removal efficiency (RE) from contaminated waters were estimated as outlined by Liu *et al.* (2020).

$$q_e = \frac{V(C_o \times C_e)}{m} \qquad \text{Eq 1}$$

$$RE = \frac{C_e \times C_o}{C_o} \times 100 \qquad \text{Eq 2}$$

where C_o is Cd concentration at the zero time and C_e is Cd concentration at the adsorption time. V is the volume of the solution, and m is the dried weight (g) of used Fe enriched biochar. Removal efficiency data were subjected to one- way ANOVA and Dunken's text via SPSS ver 18.

Kinetics of Cd sorption was also investigated via fitting Cd sorption ageing to 4 kinetic models as introduced by Zafar *et al.* (2015).

TABLE 1. Kinetic models used in the current investigation

Kinetic model	Parameters
Logarithmic law rate Q_t=aln(t-t_0)	a & b are constants
Power function: $Q_t = at^b$	a , initial metal fixation rate constant b , fixation rate coefficient
Pseudo 1st order: $Q_t=Q_e(1-e^{-k_1 t})$	K_1 : the pseudo-first order constant Q_e: adsorption capacity at equilibrium
Pseudo 2nd order: $Q_t = \frac{k_2 Q_e^2 t}{1+k_2 Q_2 t}$	k_2: the pseudo-second order constant Q_e: adsorption capacity at equilibrium

Standard error of estimate (S.E.) was calculated as outlined by Shariatmadari (2006)

$$SE = [\sum (Q_t - Q_t')^2 / (n-2)]^{1/2} \qquad \text{Eq 3}$$

Q_t and Q_t' are the measured and predicted concentrations of sorbed Cd at time t, respectively, while n is the number of measurements.

3. Results and Discussion

3.1. Concentrations of Cd in the aqueous solution as affected by application of biochar enriched with Fe and ageing

Application of biochar enriched with Fe lessened considerably Cd concentrations in the aqueous solution within one hour of application (60 min) while remained steadily unchangeable till the end of the experiment (Fig 1). This result indicates that biochar had high affinity for Cd sorption, mainly on the oxygen-containing functional groups (Yang *et al.*, 2022).

Also this process might form iron plaque which increase its sorption binding sites to sorb more Cd (Yang *et al.*, 2022). Sorption of Cd was then calculated and presented in Fig 2.

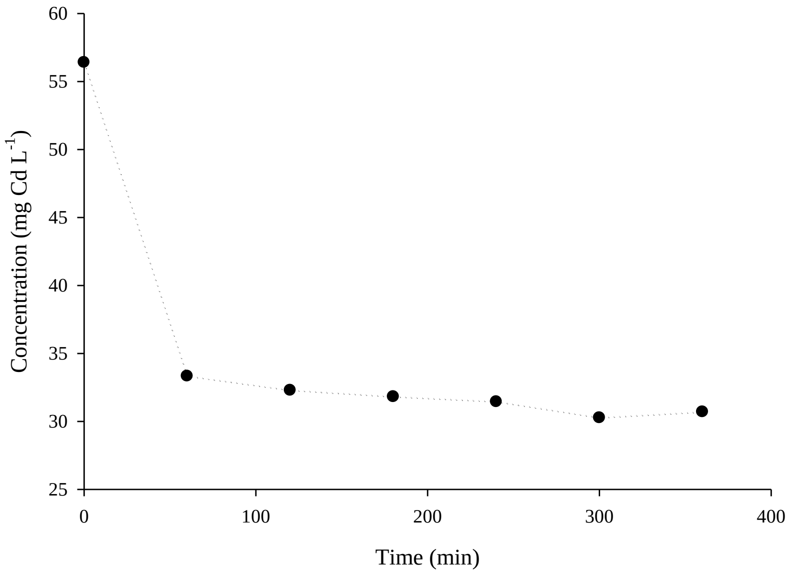

Fig 1. Effect of amending biochar amended with Fe on the soluble concentrations of Cd in aqueous solution

3.2. Sorption kinetics of Cd from aqueous solutions on biochar enriched with Fe

A rapid initial increase occurred in sorbed Cd on surfaces of biochar enriched with Fe within the first 60 min of application; thereafter sorption rate decreased noticeable. Anyhow, Cd sorption kinetics was fitted to 4 mathematical models, i.e. power function, exponential pseudo first order, logarithm and pseudo 2^{nd} order models (Fig. 2). The calculated r^2 values and standard error of estimates for the applied mathematical models are presented in Table 2.

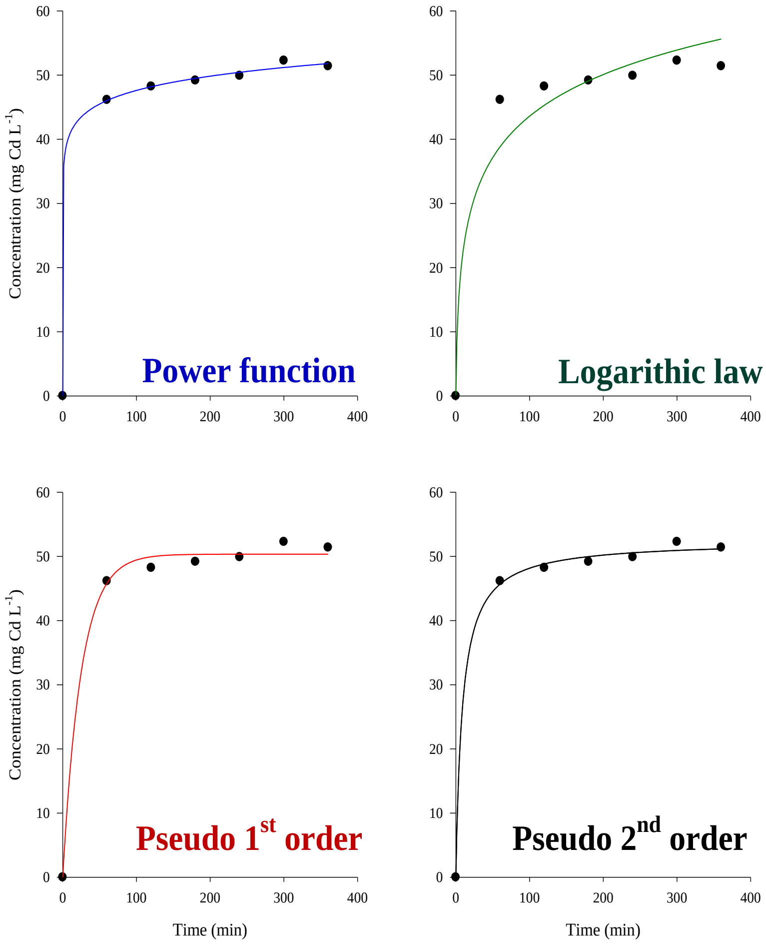

Fig 2. Kinetics of Cd sorption from aqueous solutions by biochar enriched with Fe

Based on the highest r^2 value and the least standard error of estimates, the power function was the best model fitting Cd sorption ageing in soil. This type of sorption was thought to be controlled chemically, i.e. precipitation and complexation are the main mechanisms (Yang *et al.*, 2022) In this concern, Fe oxides increased Cd binding (Yang *et al.*, 2022) and generally different iron components took part in its sorption (Yuan et al., 2020). During this process, valence of Fe_2O_3 changed in biochar enriched with Fe during Cd sorption (Yang *et al.*, 2022). In a study made by Yang *et al.* (2021), Cd sorption on Fe-Zn composite modified biochar followed the pseudo 2^{nd} kinetic model

TABLE 2. Correlation coefficients (r^2) and standard error of estimates (SEE) calculated for Cd sorption fittings

	Power	Pseudo 1^{st} order	Logarithm	Pseudo second order
model	$Q_t=at^b$	$Q_t=Q_e(1-e^{-k_1 t})$	$Q_t=a\ln(t-t_0)$	$: Q_t = \frac{k_2 Q_e^2 t}{1+k_2 Q_2 t}$
R2	0.999	0.996	0.960	0.998
Standard error of estimates	0.5880	1.368	1.8369	0.837

3.3. Removal efficiency of Cd via Fe enriched biochar

The efficiency of Fe enriched biochar to remove Cd from aqueous solutions was calculated and presented in Fig 3. It was found that this efficiency increased slightly; however significantly with ageing. By the end of the experimental period, this efficiency was estimated by about 46% of the soluble Cd. This rate was much higher than the ones found by Yang *et al.* (2021) (i.e. 17%) and Yang *et al.* (2022) (i.e. 20-30%)

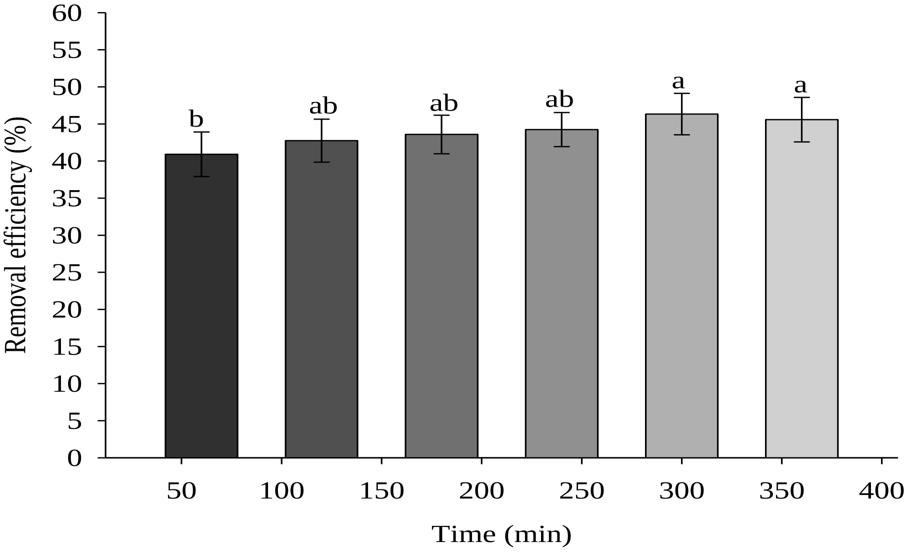

Fig 3. Removal efficiency of Cd from aqueous solutions by biochar enriched with Fe. Similar results indicate no significant variations among treatments

4. Conclusions

A rapid initial increase occurred in sorbed Cd on surfaces of biochar enriched with Fe within the first 60 min of application; thereafter sorption rate decreased noticeable. In this aspect, biochar enriched with Fe removed up to 46% of the soluble Cd within this period. This type of sorption fitted the power function kinetic model and is thought to be controlled chemically. Overall, the removal efficiency was not enough (only 46%) to attain successful removal of Cd from wastewater, at least in presence of this additive solely within short time periods. Long term experiments might also help to find out the maximum efficiency that Fe enriched biochar may achieve for removal of Cd from wastewater

5. Conflicts of interest

There are no conflicts to declare.

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This research received no public fund

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7. References

Abdelhafez AA, Li J, Abbas MHH (2014) Feasibility of biochar manufactured from organic wastes on the stabilization of heavy metals in a metal smelter contaminated soil. Chemosphere 117, 66-71. https://doi.org/10.1016/j.chemosphere.2014.05.086

Abdelhafez AA, Zhang X, Zhou L, Cai M, Cui N, Chen G, Zou G, Abbas MHH, Kenawy MHM, Ahmad M, Alharthi SS, Hamed MH (2021) Eco-friendly production of biochar via conventional pyrolysis: Application of biochar and liquefied smoke for plant productivity and seed germination. Environmental Technology & Innovation 22, 101540. https://doi.org/10.1016/j.eti.2021.101540

Bassouny M, Abbas MHH (2019) Role of Biochar in Managing the Irrigation Water Requirements of Maize Plants: the Pyramid Model Signifying the Soil Hydro-physical and Environmental Markers. Egyptian Journal of Soil Science 59, 99-115. https://doi.org/10.21608/ejss.2019.9990.1252

Chen G, Wang C, Tian J, Liu J, Ma Q, Liu B, Li X (2020) Investigation on cadmium ions removal from water by different raw materials-derived biochars. Journal of Water Process Engineering 35, 101223. https://doi.org/10.1016/j.jwpe.2020.101223

Dad FP, Khan W-u-D, Tanveer M, Ramzani PMA, Shaukat R, Muktadir A (2021) Influence of iron-enriched biochar on Cd sorption, its ionic concentration and redox regulation of radish under cadmium toxicity. Agriculture 11, 1. https://doi.org/10.3390/agriculture11010001

Đukić-Ćosić D, Baralić K, Javorac D, Djordjevic AB, Bulat Z (2020) An overview of molecular mechanisms in cadmium toxicity. Current Opinion in Toxicology 19, 56-62. https://doi.org/10.1016/j.cotox.2019.12.002

Farid IM, Siam HS, Abbas MHH, Mohamed I, Mahmoud SA, Tolba M, Abbas HH, Yang X, Antoniadis V, Rinklebe J, Shaheen SM (2022) Co-composted biochar derived from rice straw and sugarcane bagasse improved soil properties, carbon balance, and zucchini growth in a sandy soil: A trial for enhancing the health of low fertile arid soils. Chemosphere 292, 133389. https://doi.org/10.1016/j.chemosphere.2021.133389

Halttunen T, Salminen S, Tahvonen R (2007) Rapid removal of lead and cadmium from water by specific lactic acid bacteria. International Journal of Food Microbiology 114, 30-35. https://doi.org/10.1016/j.ijfoodmicro.2006.10.040

Hamzenejad Taghlidabad R, Sepehr E, Khodaverdiloo H, Samadi A, Rasouli-Sadaghiani MH (2020) Characterization of cadmium adsorption on two cost-effective biochars for water treatment. Arabian Journal of Geosciences 13, 448. https://doi.org/10.1007/s12517-020-05477-6

Hayat MT, Nauman M, Nazir N, Ali S, Bangash N (2019) Environmental Hazards of Cadmium: Past, Present, and Future. In: Hasanuzzaman, M., Prasad, M.N.V., Fujita, M. (Eds.), Cadmium Toxicity and Tolerance in Plants. Academic Press, pp. 163-183. https://doi.org/10.1016/B978-0-12-814864-8.00007-3

Islam MS, Magid ASIA, Chen Y, Weng L, Ma J, Arafat MY, Khan ZH, Li Y (2021) Effect of calcium and iron-enriched biochar on arsenic and cadmium accumulation from soil to rice paddy tissues. Science of The Total Environment 785, 147163. https://doi.org/10.1016/j.scitotenv.2021.147163

Khalil FW, Abdel-Salam M, Abbas MHH, Abuzaid AS (2023) Implications of Acidified and Non-Acidified Biochars on N and K Availability and their Uptake by Maize Plants. Egyptian Journal of Soil Science 63, 101-112. https://doi.org/10.21608/ejss.2023.184654.1560

Kumar S, Sharma A (2019) Cadmium toxicity: effects on human reproduction and fertility. Reviews on Environmental Health 34, 327-338. https://doi.org/10.1515/reveh-2019-0016

Liu Z, Lu C, Yang S, Zeng J, Yin S (2020) Release characteristics of manganese in soil under ion-absorbed rare earth mining conditions. *Soil and Sediment Contamination: An International Journal* **29**, 703-720, https://doi.org/10.1080/15320383.2020.1771273

Mohamed I, Farid IM, Siam HS, Abbas MHH, Tolba M, Mahmoud SA, Abbas HH, Abdelhafez AA, Elkelish A, Scopa A, Drosos M, AbdelRahman MAE, Bassouny MA, (2024) A brief investigation on the prospective of co-composted biochar as a fertilizer for Zucchini plants cultivated in arid sandy soil. Open Agriculture 9. https://doi.org/10.1515/opag-2022-0322

Puglla EP, Guaya D, Tituana C, Osorio F, García-Ruiz MJ (2020) Biochar from Agricultural by-Products for the Removal of Lead and Cadmium from Drinking Water. Water 12, 2933. https://doi.org/10.3390/w12102933

Pyrzynska K (2019) Removal of cadmium from wastewaters with low-cost adsorbents. Journal of Environmental Chemical Engineering 7, 102795. https://doi.org/10.1016/j.jece.2018.11.040

Raj D, Maiti SK (2020) Sources, bioaccumulation, health risks and remediation of potentially toxic metal(loid)s (As, Cd, Cr, Pb and Hg): an epitomised review. Environmental Monitoring and Assessment 192, 108. https://doi.org/10.1007/s10661-019-8060-5

Rani A, Kumar A, Lal A, Pant M (2014) Cellular mechanisms of cadmium-induced toxicity: a review. International Journal of Environmental Health Research 24, 378-**399. https://doi.org/10.1080/09603123.2013.835032**

Tolba M, Farid IM, Siam H, Abbas MHH, Mohamed I, Mahmoud S, El-Sayed AE-K (2021) Integrated Management of K -Additives to Improve the Productivity of Zucchini Plants Grown on a Poor Fertile Sandy Soil. Egypt J Soil Sci 61, 355-365. https://doi.org/10.21608/ejss.2021.99643.1472

Yang T, Xu Y, Huang Q, Sun Y, Liang X, Wang L (2022) Removal mechanisms of Cd from water and soil using Fe–Mn oxides modified biochar. Environmental Research 212, 113406. https://doi.org/10.1016/j.envres.2022.113406

Yang T, Xu Y, Huang Q, Sun Y, Liang X, Wang L, Qin X, Zhao L (2021) Adsorption characteristics and the removal mechanism of two novel Fe-Zn composite modified biochar for Cd(II) in water. Bioresour Technol 333, 125078. https://doi.org/10.1016/j.biortech.2021.125078

Yuan S, Hong M, Li H, Ye Z, Gong H, Zhang J, Huang Q, Tan Z (2020) Contributions and mechanisms of components in modified biochar to adsorb cadmium in aqueous solution. Sci Total Environ 733, 139320. https://doi.org/10.1016/j.scitotenv.2020.139320

Zafar S, Khalid N, Daud M, Mirza ML (2015) Kinetic studies of the adsorption of thorium ions onto rice husk from aqueous media: Linear and nonlinear approach. The Nucleus 52, 14-19.

Zhang X, Zou G, Chu H, Shen Z, Zhang Y, Abbas MHH, Albogami BZ, Zhou L, Abdelhafez AA (2023) Biochar applications for treating potentially toxic elements (PTEs) contaminated soils and water: a review. Front. Bioeng. Biotechnol. 11. https://doi.org/10.3389/fbioe.2023.1258483

Zhao D, Wang P, Zhao F-J (2023) Dietary cadmium exposure, risks to human health and mitigation strategies. Crit Rev Environ Sci Technol. 53, 939-963. https://doi.org/10.1080/10643389.2022.2099192