Egyptian Journal of Soil Science

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Are Normal and N-doped Hydrochars Efficient Enough for Removal of Pb(II) from Contaminated Waters?

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WATER pollution possesses a potential threat to the surrounding ecosystem. Thus, the current study investigates the efficiency of using two safe organic products, named hydrochar and N-doped hydrocar for removal of Pb(II) from contaminated waters. To attain this aim, sugarcane bagasse was collected then pyrolyzed (+/-NH_3) in an electric furnace at 200 ℃ for 24 h. Thereafter, the efficiency of each organic product for removal of Pb(II) from a water artificially polluted with Pb(II) (55 mg Pb L^{-1}) was tested individually. These hydrochars were added at a rate of 0.25g to purify 500 mL of contaminated water. Throughout the experimental period, water samples were collected periodically at 13 time periods starting from the zero time up to 360 min of contact with 30 min time intervals. Key results indicate that application of hydrochar remarkably diminished soluble Pb(II) concentrations. In this concern, Pb(II) sorption occurred from the beginning of contact with experiment up to 150 min of contact, recording approximately 70% Pb(II) removal efficiency. Thereafter significant increases in soluble Pb(II) occurred, which accounted for about 50% of the sorbed Pb(II) amount. On the other hand, N-doped hydrochar lessened considerably Pb sorption (≈3 folds) and, at the same time, accelerated its desorption. Kinetics of Pb(II) desorption by using both types of hydrochars followed the inverse third-order model. These results supported our main hypothesis, while raises doubts about the feasibility of using hydrochars for successful decontamination of waters polluted with Pb(II). Future perspectives are needed to find out better modifications of hydrochar for effective removal of contaminants from wastewaters and investigate the mechanisms beyond their modes of action.

Keywords: Hydrochar, N-dopped hydrochar, lead contamionation, Pb(II) desorption kinetics.

1. Introduction

Water is a crucial ingredient of the whole ecological system (Salam 2024; Sári *et al*. 2024). For mankind, it is an important component to attain the US sustainable developmental goals (Mujtaba *et al.* 2024). Despite that, the main challenge is to supply safe drinking water for 6.9 billion of population around the world (Oelkers *et al*. 2011), and there appears to be a gap between available fresh water and human population growth (Qureshi 2020; Saquib *et al.* 2022). Actually, 80% of the world population suffer from fresh water scarcity (Scanlon *et al.* 2023) and maybe the conflict over water could direct 'water wars' in the next few years (Biswas and Tortajada 2019).

Another global threat is unsafe drinking water which leads to death of approximately 485,000 of the world population annually (Zhang *et al.* 2023), especially in low- and middle-income countries (Jury and Vaux, 2007; Lee *et al.* 2023). Accordingly, effective alarming systems should be run to follow up changes in water quality and safety (Ateia *et al*. 2024). In this aspect, potentially toxic elements (PTEs) are of particular anxiety (Abbas *et al*. 2015 & 2017; Hussain *et al*. 2020; Farid-ul-Haq *et al*. 2021; Sarhan *et al*. 2021; Ali *et al*. 2023; Abd-El-Hady and Abdelaty 2022; El-Shwarby *et al*. 2022; Belal et al 2024) because PTEs are non-biodegradable; hence, have accumulative nature (Ali *et al*. 2023; Dehghani *et al*. 2023).

Lead (Pb) is among these contaminants which causes "serious damage to the central nervous system, reproductive system, liver, and kidney (Dehghani *et al*. 2023)", even at small concentrations (Wu *et al*. 2023).Thus, effective remediation/treatment protocols should be followed to avoid the indirect negative impacts of wastewaters on the surroundings. For example, these wastewaters may come in contact with fresh water

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Received: 10/09/2024; Accepted: 16/10/2024
DOI: 10.21608/EJSS.2024.319772.1855

bodies in nearby areas via hydraulic continuity causing disasterious ecological impacts (Bassouny *et al.* 2020; Farid *et al.* 2020).

Various methods are suggested for water remediation, such as "chemical precipitation, ion exchange, reverse osmosis, membrane filtration, bio absorption, adsorption methods and phytoremediation" (Lodhi *et al.* 2019; Panneerselvam and Priya K 2023). Biochar and hydrochar are among the sustainable, ecofriendly and economical additives that follow circular economy (Padhye *et al.* 2022) in converting organic residues into valuable products (Wu *et al.* 2021; Islam *et al.* 2022). These products can then be used in environmental remediation and also to mitigate climate change (Zhang *et al.* 2021).

Production of hydrochar takes place through pyrolyses of organic wastes at high temperature in presence of water (Azzaz *et al.* 2020; Kaboggoza *et al.* 2024) and self generated pressure (above saturated vapor pressure) (Merzari *et al.* 2020). This may save energy-intensive pre-drying (Jalilian *et al.* 2024). Hydrochar acts as an adsorbent that can remove considerable concentrations of nutrients (Wu *et al.* 2021) and potentially toxic elements from wastewaters (Babeker and Chen 2021). Aditionally, their PTEs contents seemed to be of relatively high degree of stability (Liu *et al.* 2023). In this aspect, hydrochar efficiency for removal of Pb could reach 78% (Adebisi *et al.* 2016). Probably, activating surface functional groups through chemical/physical methods may further improve hydrochar efficiency as an adsorbent (Jalilian *et al.* 2024). For example, iron modified hydrochar increase its capability to sorb more potentially toxic elements such as As(Zhang *et al*, 2024), Cr (Cui *et al.* 2024), Pb and Sb (Teng *et al.* 2020). N-doped hydrochar is another modification that may also help in removal of considerable concentrations of PTEs from wastewaters (Leng *et al.* 2020; Wang *et al.* 2023), such as Pb(II), Cd (II)(Khan *et al.* 2019), Cu(II) and Cr(VI) (Kim *et al.* 2023). Its efficcieny for removing Pb from aqueous solutions was estimated by 80% (Li *et al.* 2022). There is a lack of studies regarding hydrochar applications as amendments to improve the surrounding environment (Masoumi *et al.* 2021), especially the N-doped type in the remediation field of wastewaters. Thus, the current study investigates the efficiency of using both hydrochar and N-doped hydrocar individualy for removal of Pb(II) from contaminated waters.

Distinctively, we anticipate that hydrochar could remove considerable concentrations of Pb(II) from wastewater with high efficiency, yet Pb(II) ions might not be strongly bond to the surface functional groups of N-doped hydrochar. This is because Pb(II) is sorbed as a an outer sphere complex, in the form of a monolayer as mentioned by Koprivica *et al.* (2023). On the other hand, NH_4^+ ions are specifically sorbed on organic sorbents (Hu *et al.* 2020) and if traces of NH_4^+ ions still existed in doped hydrochar, then these ammonium ions could substitute surface bond cations such as Pb(II). Moreover, N-based functional groups are specific mainly for adsorption of anionic species (Kasera *et al.* 2022) and more than 93% of the soluble Pb(II) in wastewater exists in the form of positively charged ions (Yamada and Katoh 2020). Our assumption may therefore contradict the findings of many researchers, consequently kinetics of Pb(II) sorption/desorption on these sorbents were a matter of concern in this study.

2. Materials and Methods

2.1.1. Preparation of Pb(II) contaminated water

Lead acetate trihydrate (≥99% Sigma Aldrich) was dissolved in double distilled water (ddH_2O) for preparation of a solution, containing 55.5 mg Pb L^{-1}. Sugarcane bagasse(BG) was collected from the nearby juice bars, washed with distilled water and dried at 70° C for 48 h. Thereafter, plant residues were crushed, and divided into two equal parts. The first portion was mixed in a Teflon vessel with distilled water at a rate of 1:10, , then placed in an electric furnace at 200 C for 24 h. Thereafter, the organic product was washed with distilled water, filtrated then oven dried at 55°C. The second part was prepared as mentioned above; yet plant residues were dipped in ammonia chloride solution rather than distilled water prior to being placed in the electric furnace (Li *et al.* 2021) Schem 1 .

2.1.3. Characteristics of hydrochars under investigation

The SEM images of studied hydrochars exhibit substantial modifications in their surface morphologies (Fig 1). It seems that N-dopped hydrochar (Fig 1B) was less compacted than the normal hydrochar (Fig 1A).

Multipoint BET method was applied to determine the surface area of the two types used hydrochars (Fig 1 C & D) and the results are presented in Table 1. It seems that the N-doped hydrochar exhibited lower surface area than the corresponding one of normal hydrochar. This might be because hydrochars contained higher oxygen rich functional groups than N-doped hydrochars (Table 2).

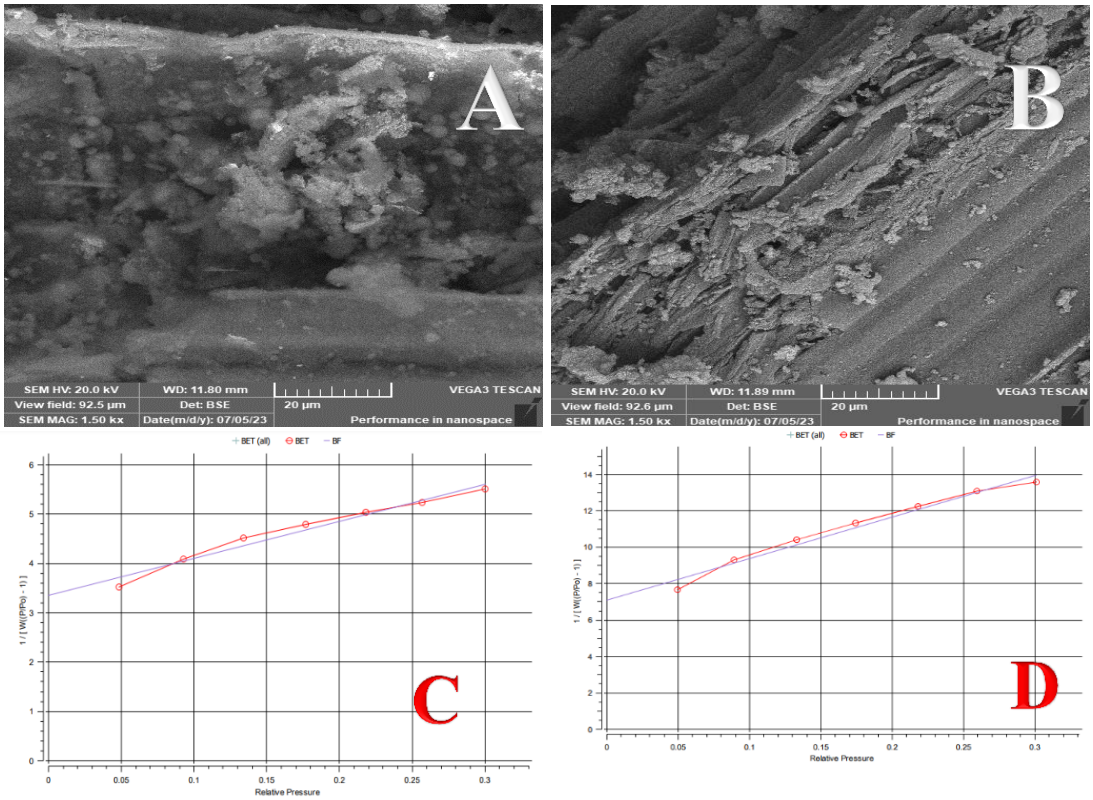


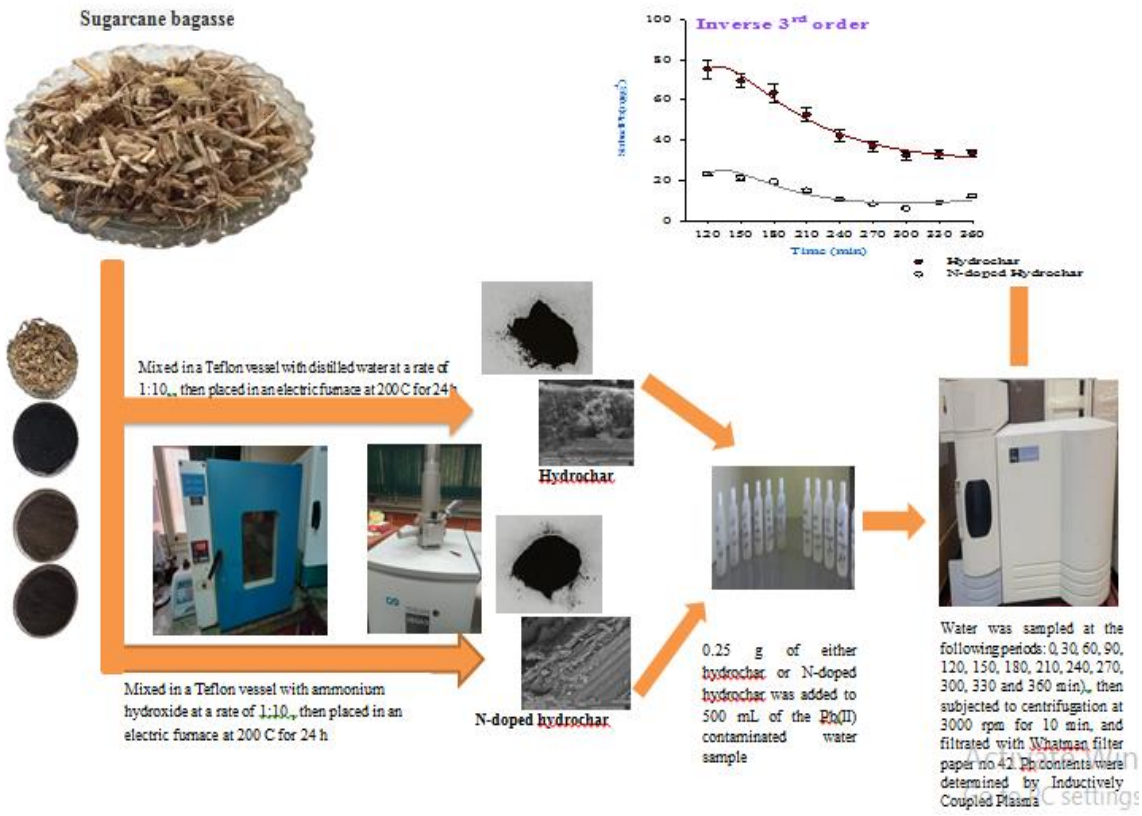
Fig. 1. SEM images (A: hydrochar and B: doped hydrochar) and BET Multi-point graphs (C: hydrochar and D: doped hydrochar).

Table 2. Element analysis of the investigated hydrochars.

Organic product	Element Content (%)				Atomic ration			Surface area (m^2 g^{-1})
	C	H	N	O	O/H	H/C	(O+N)/C	
Hydrochar	65.89	5.601	13.83	14.679	2.62	0.085	0.433	320.443
N-doped hydrochar	69.4	6.652	17.802	6.146	0.92	0.096	0.345	116.1

2.2. The experimental study

Seventy eight centrifuge cups were filled with 500 mL of water artificially contaminated with Pb(II). These waters received either hydrochar or N-doped hydrochar at a rate of 1: 2000 (0.25 g: 500 mL of the Pb(II) contaminated water sample). All tubes were then agitated, while being sampled (3 replicates) at the following periods: 0, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330 and 360 min). Samples were then subjected to centrifugation (SC-3610, Changzhou, China) at 3000 rpm for 10 min, and filtrated with Whatman filter paper no 42. Pb contents in the filtrate were determined by Inductively Coupled Plasma *(ICP-OES Perkin Elmer 5300 DV*).



Schem 1. Diagram for the experimental procedure.

2.3. Data processing

Graphs were plotted using Sigma Plot 10 software. Removal efficiency data of Pb(II) was calculated according to Liu *et al*. (2020) as shown below

$$R\% = \frac{C_0 - C_e}{C_0} 100 \qquad (1)$$

Calculated data were subjected to one way anova and Duncan multiple range tests using SPSS 18 statistical software.

Sorption capacity was calculated according to Liu et al. (2020) as follows.

$$q_e = \frac{V(C_o \times C_e)}{m} \qquad (2)$$

where C_o and C_e are the initial and subsequent concentrations of Pb(II) determined at the studied sampling periods, in a solution of volume (v), after adding (m) grams of hydrochar (on dry bases). All chemicals of the study were of analytical grade.

Kinetics of Pb(II) desorption were then fitted to 4 kinetic models, i.e. inverse first order, inverse second order, inverse third order and exponential decay model. Standard error of estimate (S.E.) was calculated as outlined by Shariatmadari (2006)

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

Where Q_t and Q_t' are the measured and predicted concentrations of sorbed Pb(II) at time t, respectively, while n is the number of measurements.

3. Results

3.1. Characterization of the used hydrochars

Adsorption peaks of FTIR were detected at <1000, 3000 and 3700 $cm^{-1}$and the broad band peak was seen around 1750 cm^{-1}. The functional groups at frequency range (cm-1): 600-700 (C-H linkage), 1000 (C-N groups) (Chen *et al.* 2022), around 1700 (C=O stretching), 2080 (NH_2 peak) (Arief *et a*l. 2008), 3000 (C-H stretching) (Dong *et al.* 2019). Probably, higher band peak (≈3700 cm^{-1}) is associated with hydroxyl (–OH) group (Khan *et al.* 2019) Fig 2 A.

Regarding the XRD chart (Fig 2 B), a wide peak was observed at 2θ≈23°, revealing the amorphous structure of the non doped type of hydrochar with NH_4Cl relative to N-doped hydrochar, or probably there were smaller crystals with defects in structure.

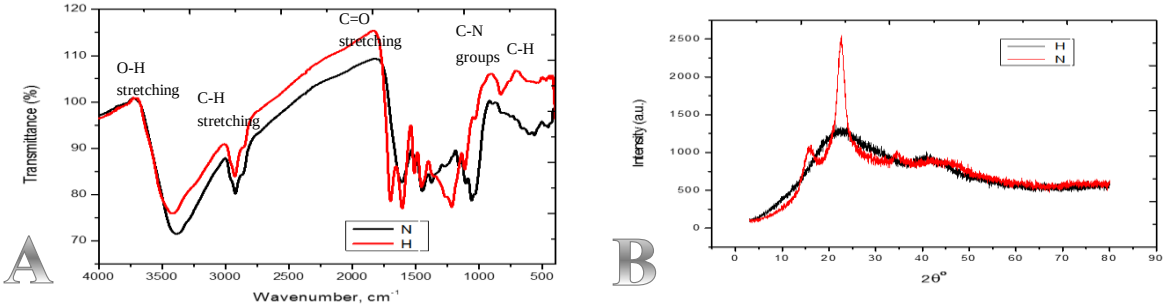


Fig. 2. FTIR spectra (A) and XRD chart (B) for both N-hydrochar (black beak) & hydrochar (red peak).

3.2. Removal of Pb(II) from decontaminating water by hydrochars

Application of hydrochars (+/- N-doping) remarkably diminished Pb(II) concentrations in contaminated water; yet within only short time periods; thereafter significant increases occurred (Fig 3). The reductions in Pb(II) concentrations were distinguished as Pb sorbtion which lasted for 150 min of contact when using non-doped hydrochar with N as an adsorbent, while remained only 60 min when using N-doped hydrochar. On the other hand, the re-rise in Pb(II) soluble concentrations were remarked as Pb(II) desorption. These results signify that the presence of NH_4^+ in hydrochar lessened considerably Pb(II) sorption and, at the same time, accelerated its release back to the solution.

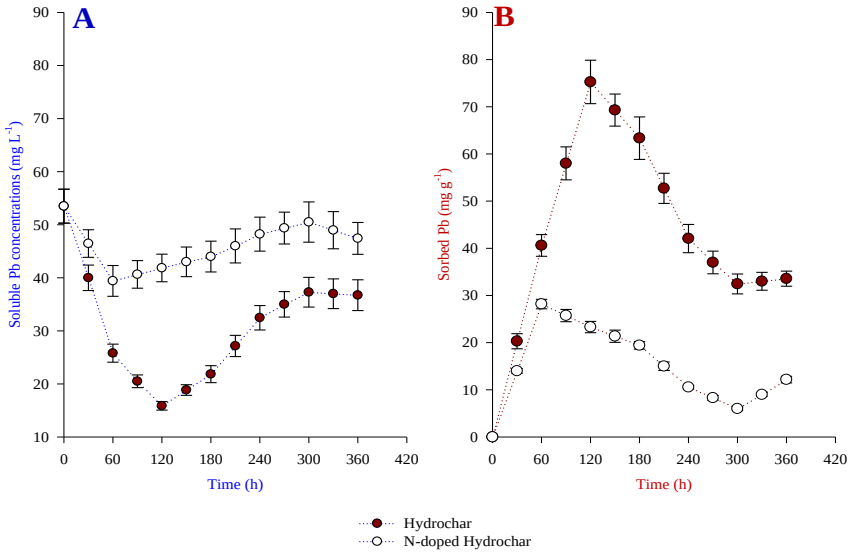


Fig. 3. Kinetics of Pb(II) sorption/desorption on hydrochar surfaces (mean±standard deviation).

Removal efficiencies of Pb(II) due to application of hydrochars (+/- NH_4^+) were then calculate and presented in Fig. 4. Results revealed that these efficiencies increased significantly within short time periods of contacts; thereafter decreased noticeably. The increases in removal efficiencies of Pb(II) continued up to 120 min with hydrochar application, recording approximately 70%; while the corresponding increases in removal efficiencies of Pb (II) in case of N-doped hydrochar took only 60 mins and removed about 25% of soluble Pb(II). Notably

about 50% of the sorbed Pb(II) by the two types of hydrochars returned back to the solution in soluble forms by the end of the experimental period. Overall, non-doped hydrochar with NH_4^+ removed higher Pb(II) concentration (≈3 fold) than that removed by hydrochar which was doped with NH_4^+.

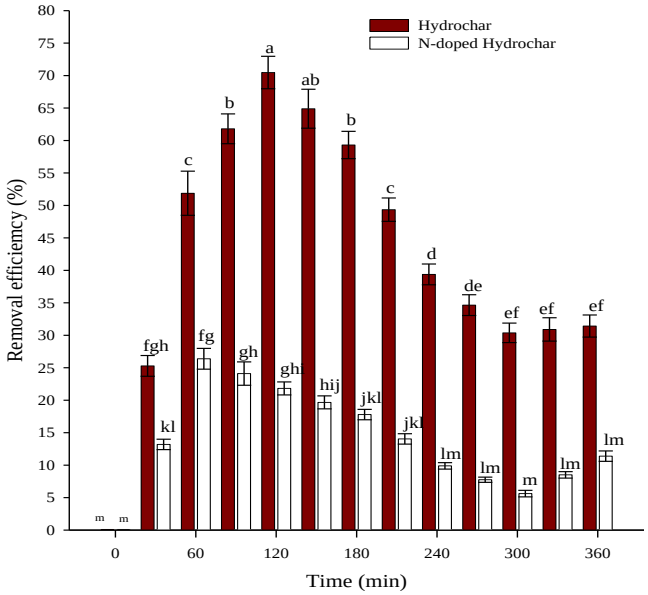


Fig. 4. Removal efficiencies of Pb (II) from contaminated waters by hydrochars (mean±standard deviation). No significant variations among similar letters.

3.2. Desorption kinetics of Pb(II) on hydrochars

Desorption kinetics data of Pb(II) were fitted to 4 mathematical methods, i.e. inverse 1st order, inverse 2nd order, inverse 3rd order and exponential decay (Fig 5) and the results are presented in Table 2.

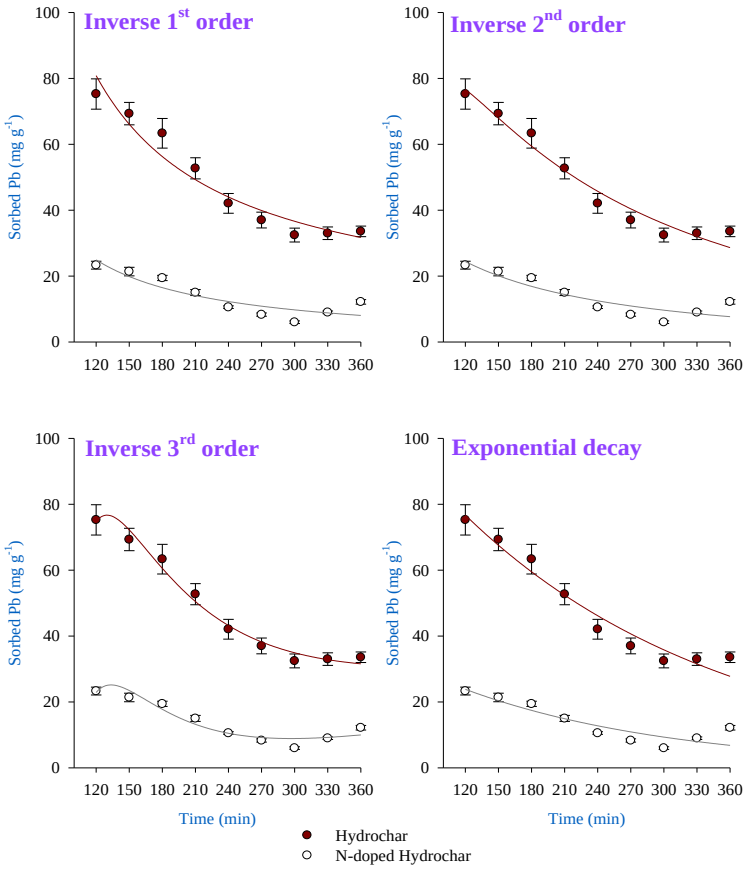


Fig. 5. Kinetics of Pb (II) desorption (mean±standard deviation)from hydrochars.

Table 2. Correlation coefficients (r^2), standard error of estimates (S.E.) and calculated parameters for the fittings of Pb(II) sorption kinetics on hydrochars.

	Inverse 1st order $Q_t=Q_0+a/t$	Inverse 2nd order $Q_t= Q_0+a/t+b/t^2$	Inverse 3rd order $Q_t= Q_0+a/t+b/t^2+c/t^3$	Exponential decay $Q_t= a\times e^{-bt}$
		Hydrochar		
r^2	0.940	0.9642	0.9849	0.9575
Standard error of estimates	4.426	3.69	2.626	3.7226
Calculated parameters	Y0=7.160	Y0=-15.677	Y0=63.367	A=127.41
	A=8840.802	A=1839.048	A=-31454.107	B=0.0042
		B=-877886.367	B=8836110.458	
			C=-587835941	
		N-doped Hydrochar		
r^2	0.822	0.8248	0.950	0.813
Standard error of estimates	2.797	2.9974	2.216	2.865
Calculated parameters	Y0=-0.380	Y0=-3.1889	Y0=59.125	A=44.526
	a=3036.374	a=4211.460	A=-35086.328	B=0.0052
		b=-107983.39	B=7550044.837	
			C=-463420392.155	

The highest r^2 values and the least standard error of estimates were calculated for the inverse 3rd order and therefore this model best fitted the rate limiting step for Pb(II) desorption from the two types of hydrochar.

4. Discussion

4.1. Removal of Pb(II) by non-doped hydrochar with $NH4^+$

Addition of hydrochar to Pb(II) contaminated water removed temporarily considerable amounts of Pb(II) within the first 120 min of contact, and this amount was estimated by 70% of the Pb(II) contamination level. Probably, Pb(II) ions were bound to the negativly charged carboxyl and –OH functional groups on hydrochar surfaces (Malool *et al.* 2021).

The maximum adsorption of Pb(II) obtained herein (75.6 mg Pb g^{-1}) was comparable to the maximum adsorption capacities of hydrochar obtained by many researchers, i.e. 22.82 mg Pb g^{-1} for peanut hulls biochar modified by H_2O_2 (Xue *et al.* 2012), 45.3 mg Pb g^{-1} for the African prospis shell hydrochar (Elaigwu *et al.* 2014), 62.4 mg Pb g^{-1} for modified sewedge sludge hydrochar (Luo *et al*. 2020) and 92.24 mg Pb g^{-1} for sugarcane bagasse alkali modified hydrochar (Malool *et al*. 2021).

On the other hand, more than 50 % of the sorbed Pb(II) were set back to the solution and this might indicate that Pb(II) ions were weakly bound via outer sphere complexes on hydrochar surfaces and these ions could be easily substituted by other ions in the solution (Zhao *et al.* 2021). Probably,the increases in sorption of metal ions such as Pb(II) on organic complexes, forming a swarm of crowded electrons which become unstable. This increased its dissociation rate part by part until ion-organic complexes re-gained their stability (Wang *et al.* 2016). Some of the dissociated organic fractions could be of low molecular weight soluble Pb(II) organic-complexes(Qin *et al.* 2004; Spitzer and Poolman 2009). Another scenario for the increases that occurred in Pb(II) desorption after 120 min of contact is that many ions were set free during partial dissociation of hydrochar (Khosravi *et al.* 2022) and these ions could partially substitute some of the sorbed Pb(II) on biochar surfaces(Zhao *et al.* 2021).

4.2. Removal of Pb(II) by N-doped hydrochar

N-doped hydrochar did not only lessened the sorbed amount (or removal efficiency) of Pb(II) by hydrochar, but also delayed the timing to reach Pb(II) maximum sorption. The studies conducted on hydrochars were not sufficient enough to explain our findings. Anyhow, hydrochar is a type of biochar (Kosheleva *et al.* 2019) which exhibits similar sorption capacity to biochar (Takaya *et al.* 2016). Probably, N-doping increased both hydrophobic and hydrophilic properties of this organic product as well as its acidic and basic properties (Kasera *et al*. 2022), and this consequently increased the activated sites for sorption of PTEs from wastewater (Yu *et al.* 2018; Guo *et al.* 2020; Pan *et al.* 2022), mainly in the form of anions (Kasera *et al*. 2022). Neverthless, most of Pb(II) existed as cations that bound to the surface functional groups (–COOH, and –OH) of this organic product (Teng *et al.* 2020) through ion exchange (Song *et al.* 2018).

In our case, the percentage of O-containing groups decreased in N doped hydrochar while N-containing groups increased. This consequently decrease Pb(II) sorption considerably via this organic product.

Additionally, hydrochars could chelate insoluble ions found in soil, particularly Fe (Vahedi *et al.* 2022) which is the 4th dominant cation (Beard and Johnson 2004), hence increased its solubility (Vahedi *et al.* 2022). This cation (Fe^{3+}) or other tri-valent cations could compete on the bounding sites with Pb(II) as illustrated by the following equations

$$Fe_2O_3+6H^+ \leftrightarrow 2Fe^{3+} + 3H_2O$$

(Majzlan *et al.* 2004)

$$Fe_2O_3(s) + 6H^+ + 2e^- \leftrightarrow 2Fe^{2+} + 3H_2O$$ (Shi *et al.* 2013)

Although, both Fe^{3+} and Fe^{2+} can substitute Pb^{2+} on hydrochar surfaces, but with superiority for Fe III (Li *et al.* 2020). By simple calculations, a molecule of Fe_2O_3 released 2 ions of Fe^{3+} and these two Fe^{3+} ions could substitute 3 ions of Pb^{2+} and set them free; thus there is no wonder to find out that the kinetics of Pb(II) desorption followed an inverse 3rd order model

5. Conclusion and Future Prospective

Hydrochar effectively removed 70% Pb(II) from the artificially contaminated water (55 mg Pb L^{-1}) within only 120 min of contact; yet half of the sorbed Pb(II) was loosely bound to hydrochar surfaces and released it back to the solution in a soluble form. In contrast, N-doped biochar not only decreased Pb(II) removal efficiency from contaminated water, but also accelerated its desorption. These results support the main assumption which indicates that N-doped hydrochar is not the suitable choise for removal of Pb(II) from contaminated waters.

Future perspectives are needed to find out better modifications of hydrochar for effective removal of contaminants from wastewaters and investigate the mechanisms beyond their modes of action .

Declarations

Ethics approval and consent to participate

Consent for publication: The article contains no such material that may be unlawful, defamatory, or which would, if published, in any way whatsoever, violate the terms and conditions as laid down in the agreement.

Availability of data and material: Not applicable.

Competing interests: The authors declare that they have no conflict of interest in the publication.

Funding: Not applicable.

Authors' contributions: All authors contributed equally during write the original manuscript, editing and finalizing it.

Acknowledgments:

All authors would like to thank the stuff members of both Soils and Water Department, Faculty of Agriculture, Benha University (Egypt) and the Central Laboratory for Environmental Quality Monitoring, National Water Research Centre, Elkantir, Egypt for their help during the course of this study.

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