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RESEARCH ARTICLE

ASSESSMENT OF HEAVY METALS IN HYDROCHAR PRODUCED BY HYDROTHERMAL CARBONIZATION OF DAIRY MANURE

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KEYWORDS

heavy metals, dairy manure, hydrochar, hydrothermal carbonization, waste management

HIGHLIGHTS

- Content of heavy metals in hydrochar varies considerably, from 50% to 100%.
- Concentrations of heavy metals in hydrochar can be higher than those in the dairy manure.
- Concentrations of heavy metals in hydrochar are far below the regulatory level.

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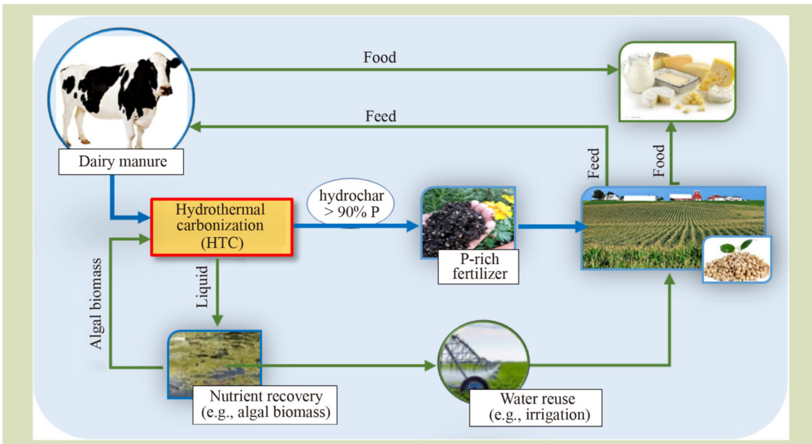
GRAPHICAL ABSTRACT



ABSTRACT

Hydrochar produced from dairy manure is a regulated biosolid if being promoted for agricultural applications thus must have the properties that comply with all environmental standards and government regulations, including the levels of heavy metals (HMs). In this study, systematic research was conducted on HM levels in hydrochar from dairy manure and on the effects of processing conditions, including processing temperature (180–255 °C), holding time (30–120 min) and solid content of manure slurry (2%–15%), through a central composite design and statistical analyses. It was found that HMs can be retained in hydrochar, ranging from 40% to 100%. The processing temperature and solid content in the feed were the most influential process parameters that affected HMs retention in hydrochar. Statistical analysis showed that there was no single optimal point to minimize HMs retained in hydrochar, but there were minimization points at given processing time and solid content. Most HMs concentrations were higher in hydrochar than those initially in dairy manure but were greatly below the thresholds as set by the US government regulations. Thus, hydrochar is feasible for use as a phosphorus-enriched organic fertilizer and/or soil amendment for agricultural applications without serious concerns about HMs it might contain.

1 INTRODUCTION

Utilizing under-utilized biomass, including agricultural residues and wastes such as dairy manure, for value-added applications is not only making our natural resources more sustainable but also benefiting the environment by offsetting the emissions of greenhouse gases and by sequestering carbon back to soil. Production of hydrochar from dairy manure is an excellent example of managing an agricultural waste in an environmentally friendly way and recycling nutrients, particularly the non-renewable phosphorus, from manures back to croplands[1,2]. However, before hydrochar can be promoted as an organic fertilizer and/or soil amendment to be applied to cropland, its characteristics, most importantly the levels of heavy metals (HMs), must be assessed.

Animal manures contain varying levels of HMs, depending on the animal type and their rations. For example, the level of lead ranges from as low as 0.63 $mg \cdot kg^{-1}$ to as high as 3.23 $mg \cdot kg^{-1}$ in cattle manure[3], 1.00 to 5.18 $mg \cdot kg^{-1}$ in dairy manure[4], and 15 to 75 $mg \cdot kg^{-1}$ in cow manure[5] as people characterize the types of manure differently. HM accumulation in animal manures leads to concerns in manure handling and storage[6–8] and in its direct land application[9], thus may pose a risk to the environment[10]. Even in manure treatment, such as anaerobic digestion and composting which are widely employed in livestock industries, HMs at high concentration are toxic to the microbial communities in the soil, potentially inhibit the microbial activity, and ultimately affect the efficiencies of manure treatments[10–12]. Additionally, the sludge from anaerobic digestion may not be appropriate for land applications at all if the accumulation of HMs in animal manures (or any biosolids) is beyond the levels set by the governmental regulations[13]. It is also unclear if manures or compost, which contain non-biodegradable HMs but are used directly for land application, present a risk to agricultural products in the food chain and thus pose a potential risk to human health[14].

Similar concerns also exist if hydrochar produced from animal manures is used as a fertilizer or soil amendment for cropland application. Hydrochar is a porous, humus-like material that can be converted from a wet biomass through hydrothermal carbonization (HTC). HTC offers significant advantages in converting wet biomass, such as raw dairy manure, for value-added uses. Unlike biochar produced from dry biomass via pyrolysis[15], hydrochar can be directly produced from wet biomass without pre-drying. Thus, HTC is a less energy-intensive way to convert wet biomass to value-added products such as hydrochar. Research has shown that hydrochar had all the characteristics and a similar quality as compost for fertilizer purposes[16]. It possesses the well-needed organic matter and nutrients, including nitrogen, potassium and especially phosphorus, best for organic farming. Hydrochar as a soil conditioner can substantially improve the soil texture and its capability of holding moisture and nutrients[17]. Additionally, hydrochar production is also a solution for organic wastes and sequestering carbon[18,19]. Manure-based hydrochar is safer to use and generally has a higher degree of acceptability by the public than raw manures due to the absence of pathogens in hydrochar[20].

Research has shown that, after biomass was converted to biochar or hydrochar by HTC, the HM levels changed considerably. Reza et al.[21] found that all HM concentrations in biochar were lower after the biomasses of corn stover, miscanthus, switch grasses and rice hulls were converted by HTC. The HM concentrations in biochar were in the ranges of 2.3–9.2, 1.8–4.8, 12.3–35.4, 4.1–14.7, 0.7–10.6, 0.5–35.2, 1.1–31.5, and 0.7–6.3 $mg \cdot kg^{-1}$ for Ni, Ag, Pb, Zn, Cu, As, Cd and Cr, respectively. However, in a study by Wang et al.[22] on a combined HTC-pyrolysis of sewage sludge, most HMs were found being amassed in the biochar, although the contents of Zn and Cd reduced from 35.0% of Zn and 20.2% of Cd in the sewage sludge to less than 19.7% and 11.8% in the biochar, respectively. Also, the processing conditions affected HM distributions in biochar considerably. In their study of urban sludge HTC, Xu and Jiang showed that the processing temperature must reach 240–300 °C in order to reduce all HM concentrations in the resultant hydrochar below acceptable levels[23]. Nevertheless, most concentrated HMs in biochar were below the allowable levels for biochar-based organic fertilizer[24]. Therefore, HM retention in biochar produced by HTC varies dramatically depending on the types of biomass and the processing conditions. Generally, HM concentrations in biochar or hydrochar are higher than those in original biomass, although some HMs are noticeably transformed into biologically stable forms under different processing conditions[22], such as CaO addition to HTC processes[10], which has the benefit of reducing the potential risk to the environment in applications.

In addition to the studies on HMs in biochar made from sewage sludges, some studies have looked at HMs in hydrochar produced from animal manures[10,25–27]. However, the information on HMs in hydrochar produced from dairy manure is lacking, especially the information on the effects of processing conditions in HTC of dairy manure. As the US Environmental Protection Agency requires that all biosolids for land applications must meet the ceiling concentrations for pollutants[13], including HMs (Table 1), an assessment of hydrochar on its HM contents is necessary to comply with the environmental laws while promoting the acceptance of hydrochar as an organic phosphorus-enriched fertilizer and/or soil amendment for agricultural applications, especially for organic farming.

In this report, we present findings on HM levels and retention rates in hydrochar produced from dairy manure under different processing conditions through an experimental central composite design (CCD) and statistical analyses. The objective of this study was to assess if the levels of HMs in hydrochar are below the thresholds set by the US government regulations under the category of biosolids and if hydrochar is feasible for use as a phosphorus-enriched fertilizer and/or soil amendment for agricultural applications.

2 MATERIALS AND METHODS

2.1 Feedstock preparation

The fresh dairy manure used in this study was collected from the floor of a dairy farm in southern Idaho and dried in batches of about 2 kg in layers in a mechanically ventilated oven at 103 °C for 24 h by following the ANSI/ASAE standard S358.3[29]. The dry manure samples were then stored in airtight containers at room temperature before used in all experiments for hydrochar production.

HM contents in the samples manure and hydrochar, along with other properties including total phosphorus, micro- and macro-elements, were analyzed for all experiments (data not shown). The contents of HMs, including arsenic, barium, cadmium, chromium, copper, lead, molybdenum, nickel, zinc were determined by the inductively coupled plasma (ICP) method, in which the samples are prepared by nitric acid digestions at 30 °C for 6 h, 70 °C for 1 h, and 120 °C for 8 h before the ICP analysis[30]. The HM contents in the dairy manure used for this study are summarized in Table 2.

2.2 Hydrochar production

Hydrochar was produced in batches by HTC conversion of dairy manure in a pressure reactor. The batch reactor (model 452HC, Parr Instruments, Peoria, IL, USA) has a capacity of 300 mL with temperature control mechanism through a proportional-integral-derivative (PID) controller (model 4848B, Parr Instruments, Moline, Illinois, USA).

Table 1 US Environmental Protection Agency regulatory determination and pollutant limits for land applied sewage sludge§

Heavy metal	Ceiling concentration ($mg \cdot kg^{-1}$)	Cumulative loading rate ($kg \cdot ha^{-1}$)	Monthly average concentration ($mg \cdot kg^{-1}$)	Annual loading rate ($kg \cdot ha^{-1} \cdot yr^{-1}$)
Arsenic*	75	41	41	2
Cadmium*	85	39	39	1.9
Chromium*	3000	3000	1200	150
Copper	4300	1500	1500	75
Lead*	840	300	300	15
Mercury*	57	17	17	0.85
Molybdenum	75	–	–	–
Nickel	420	420	420	21
Selenium*	100	100	36	5
Zinc	7500	2800	2800	140

Note: §Data extracted from reference[13]. *The RCRA 8, heavy metals regulated under the Resource Conservation and Recovery Act[28], which also includes barium and silver.

Table 2 Heavy metal contents in the dairy manure used for this study

Heavy metal*	Manure sample§		Analytical detection limit ($mg \cdot kg^{-1}$)
	Oven-dried ($mg \cdot kg^{-1}$)	Air-dried ($mg \cdot kg^{-1}$)	
Arsenic	nd	nd	40
Barium	50.3 ± 3.5	47.3 ± 3.2	0.8
Cadmium	nd	nd	0.8
Chromium	15.0 ± 1.0	18.3 ± 1.5	2
Copper	94.0 ± 4.4	88.3 ± 58.0	4
Lead	nd	nd	10
Molybdenum	nd	nd	10
Nickel	6.3 ± 0.2	6.1 ± 0.3	2
Zinc	267 ± 11.5	250 ± 10.0	2

Note: *Mercury and selenium were not tested in this study. §All data are presented as average ± standard deviation of 3 or more replicate values. nd, not detected. Concentrations of arsenic, cadmium, lead, and molybdenum were below the detection limits and are thus excluded from the table and following discussion.

Corresponding operating pressures were displayed by a transducer and a local pressure gauge but not controlled.

Manure samples with solid contents of 2%, 5%, 10% and 15% on a dry matter basis were prepared for testing in this study to reflect the practical solid contents in dairy manure from flushing systems (2%–5%) and from scraper systems (10%–15%). Operating temperatures of 180–255 °C and processing time of 30–120 min were employed. Upon the completion of an experiment, the solid product hydrochar flowing on top of the processing mixture was separated from the liquid by filtration with a filter paper (Whatman No. 4) under a medium vacuum (450–550 mmHg). The wet hydrochar after filtration was weighed and air-dried before putting in an oven at 103 °C for 24 h by following the ANSI/ASAE standard S358.3[29] to decide the moisture content and yield of the hydrochar samples.

2.3 Experimental design and data analysis

The effects of processing parameters were studied through an experimental CCD constructed by using a Microsoft Excel add-on statistical software, DOE Pro XL by SigmaZone (Orlando, Florida, USA). Three treatments, i.e., processing temperature (variable A), processing time (variable B) and solid content (variable C), each at three levels (A = 195, 215 and 235 °C; B = 30, 60 and 90 min; and C = 5%, 10% and 15%), and with one central point, were chosen and a total of 15 sets of experiments were conducted randomly in triplicate (Table 3). Each of the experimental results were analyzed using ANOVA, predictive models and HM minimization by the same Excel add-on statistical software.

2.4 Definitions of heavy metal retention rate

The analytical results on HMs in samples of dairy manure and hydrochar are given in concentrations as $mg \cdot kg^{-1}$. The HM retention rate in hydrochar after converted from manure is defined as the mass of HMs in hydrochar (mg) against that in feed manure samples (mg) in percentages on a dry matter basis:

$$p = \frac{C_h \cdot m_h}{C_m \cdot m_m} \times 100\% \qquad (1)$$

where, C_h and C_m are the concentrations ($mg \cdot kg^{-1}$) of HMs in the hydrochar and manure samples, and m_h and m_m are the masses (kg) of the hydrochar and manure samples, respectively.

3 RESULTS AND DISCUSSION

3.1 Effects of individual processing parameters

To investigate the effect of processing temperature in a wider range, a series of experiments were conducted in the temperature range 180–255 °C on HM concentrations and retention rates in the hydrochar products. Experimental results showed that as the temperature increases, the HM concentrations in hydrochar also increase proportionally (Fig. 1(a)). Depending on the types of HMs, their concentrations vary considerably but the trend was similar, with the exception of barium which remained essentially flat among all processing temperatures. The retention rates of HMs in hydrochar, however, were very high among the five detectable HMs (Fig. 1(b)), except Ba, which had a range of HM retention rates of 50%–78% as all other four HMs were in

Table 3 Process parameters in CCD and experimental results on Cr retention in hydrochar

Run no.	Process variables			Cr retention rate§ (%)	
	Temperature (A) (°C)	Time (B) (min)	Solid content (C) (%, m/m)	Average	SD
1	195	30	5	26.33	4.16
2	195	30	15	20.33	0.58
3	195	90	5	26.00	2.65
4	195	90	15	21.00	1.00
5	235	30	5	32.67	5.51
6	235	30	15	21.67	0.58
7	235	90	5	34.00	1.00
8	235	90	15	17.67	11.85
9	215	60	10	25.33	0.58
10	195	60	10	23.33	0.58
11	235	60	10	27.00	1.00
12	215	30	10	23.00	0.00
13	215	90	10	25.00	1.00
14	215	60	5	25.33	1.53
15	215	60	15	21.67	2.08

Note: §Presented as average ± standard deviation of 3 or more replicate values.

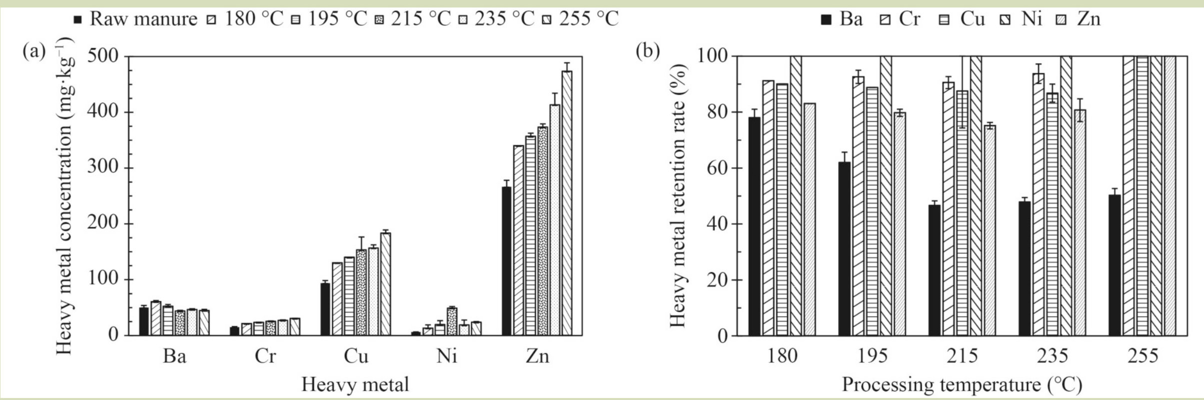


Fig. 1 Processing temperature effect on (a) concentrations and (b) retention rates of heavy metals in manure and hydrochar samples. Experiments were conducted in triplicate at 60 min of processing holding time and 10% of solid content.

75%–100%. The higher the temperature, the higher the HM retention rate. The high HM retention in hydrochar was consistent with the findings of other micro- and/or macro-minerals. This phenomenon is believed to be caused by the characteristics of hydrochar and/or biochar whose porous and matrix structures and surface characteristics can highly immobilize all types of inorganic species[18,23,30]. The higher the temperature, the more structure change in hydrochar, thus the higher the HM immobilization.

The effect of processing time also affects HM concentrations in hydrochar. As concluded in previous study, the biomass structure change mainly happened in the early stage of the HTC processing, particularly in the first 5–15 min depending on the targeted processing temperatures[31]. It was observed that the HM concentrations in hydrochar products were generally higher than that in manure, and with an increasing trend among the HMs except Ba which was slowly decreasing as the processing time increased from 30 to 120 min (Fig. 2(a)).

The HM retention rates, on the other hand, were at similar levels but did not show significant differences in the processing time range (Fig. 2(b)). It was noticed that the concentration of nickel was much lower than those of copper and zinc, but its retention in hydrochar was extremely high, almost all at 100% in the range of processing time. The other observation was that the retention of Ba was much lower (50% and less) as compared to the rest, even showing a slightly decreasing trend. Thus, despite the high HM immobilization or retention rates, HM retention in hydrochar was not significantly affected by the processing time as tested in this study. It may also imply that processing time more than 30 min is not necessary for hydrochar production as it is not beneficial in HM reduction in hydrochar.

Solid content, as presented in percentage (on a mass basis) of solid manure in the HTC slurry, represents the ratio of organic matter to the processing media or aqueous solution. The lower the solid content, the higher of the water to biomass ratio. The assumption is that the higher water to biomass ratio would lead to more rigorous leaching of minerals from biomass to aqueous phase.

The solid content in manure on dairy farms changes depending on the operations, which can be as low as 2% in flushed systems and as high as 15% (or even higher) in scraper systems. Thus, solid contents of 2%, 5%, 10% and 15% were tested in this study to mimic the scenarios in reality. It was seen that the concentrations of HMs in hydrochar decreased but all are essentially higher than that in raw manure as the solid content increased (Fig. 3(a)). This is consistent with the expected effect which is caused by the dilution or the higher ratio of aqueous solution to the solid content at lower solid contents. However, the HM retention rates were all high at 75% and above, except for Ba (Fig. 3(b)). Relatively, the retention rate of Ba was still lower as compared with others, but the trend was increasing

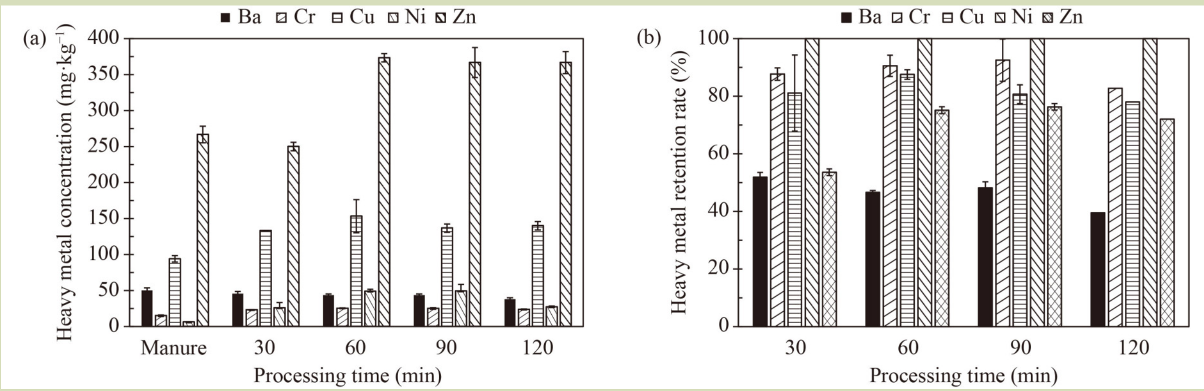


Fig. 2 Effect of processing holding time on (a) concentrations and (b) retention rates of heavy metals in manure and hydrochar samples. Experiments were conducted in triplicate at 215 °C and 10% of solid content.

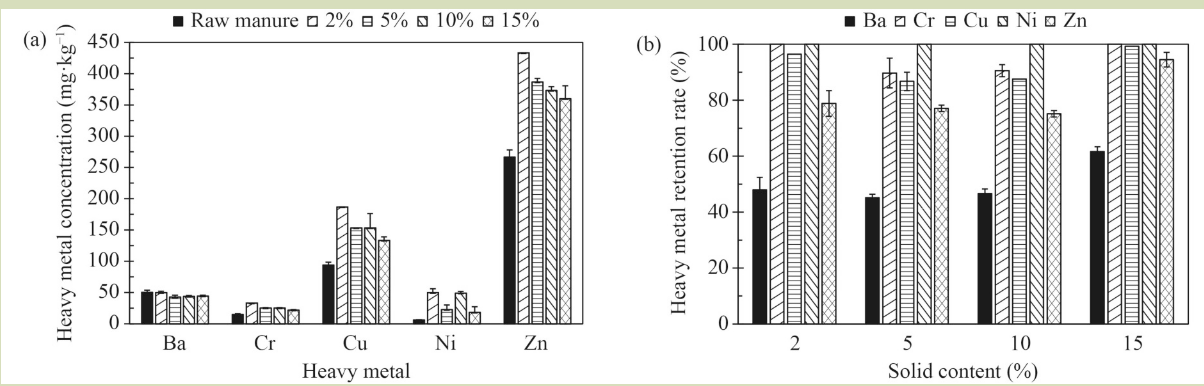


Fig. 3 Effect of solid content on (a) concentrations and (b) retention rates of heavy metals in manure and hydrochar samples. Experiments were conducted in triplicate at 215 °C and 60 min of processing holding time.

especially at 15% of solid content. This is quite different than those effects of processing temperature and time, where Ba always showed a decreasing trend. Scientifically, this is assumed to be caused by the HM concentration gradient between the solid phase and the liquid phase. In the enclosed reactor system, the working volume was fixed (approximately 160 mL), the HM concentration increased as the solid content increased, which in turn led to more HMs diffusing from solid manure into the liquid phase.

3.2 Systematic investigation of process parameters through CCD experiments

Chromium in its hexavalent form or $Cr^{(VI)}$ is very toxic and carcinogenic, and at the top list of the highly regulated HMs. Among the five detectable HMs in this study, Cr is the most important, thus was chosen as the representative element of the HMs. A series of experiments based on CCD were conducted to investigate the effects of processing conditions at which Cr was optimized for minimization in the hydrochar products. Processing temperature (variable A), processing time (variable B) and solid content (variable C) were included as the treatments in the CCD. Each treatment was set at three levels (A = 195, 215 and 235 °C, B = 30, 60 and 90 min, and C = 5%, 10% and 15%), and with one central point. The CCD construction and the experimental results on Cr retention rates in hydrochar are summarized in Table 3. ANOVA and its results are summarized in Table 4.

Based on the CCD in Table 3, the critical F value was 3.56 at $\alpha = 0.05$, indicating that the effect of a process parameter, or interactive effects of two or three treatments, would be significant if the corresponding F-value was 3.56 or greater. Table 4 reveals that solid content (variable C), with an F-value of 11.4, was the only parameter that significantly affected Cr retention in hydrochar. This effect was also reflected by the low P-value of < 0.05. It was also seen that the corresponding two- and three-way interactions with variable C (the solid content), i.e., A × C, B × C and A × B × C, were not significant, as indicated by the smaller critical F-values and larger P-values (Table 4).

However, the Y-hat prediction model analysis showed that variable A (processing temperature) did affect the Cr retention significantly, with a P-value of 0.024 (Table 5). The two-way interaction of variable A with variable C (A × C), was also significant, indicated by its small P-value of < 0.05. The F-value of 5.33 implies that the Y-hat regression model is a well-fitted statistical model for predicting the Cr retention in hydrochar.

The effects of individual process parameters and corresponding interactions can also be visually examined from the multiple plots (Fig. 4). The effects of processing temperature and time were mostly not significant as the treatments changed their levels, but not that of the variable C (solid content). Also, the effects of processing temperature and time were parallel and no evident tendency deviate from this. However, variable C clearly showed a different trend from the processing temperature and time (Fig. 4). Therefore, ANOVA concluded that the solid content and processing temperature were significant, and processing time was not significant in affecting the Cr retention in the hydrochar produced from dairy manure. The interactive effect between the processing temperature and solid content (A × C) was significant but not the other interactions between

Table 4 ANOVA of process parameters on Cr retention rates in hydrochar

Source	SS	df	MS	*F*	*P*	Concentration (%)
Processing temperature (A)	85.5	2	42.8	1.84	0.1871	7.1
Holding time (B)	0.2	2	0.1	0.0049	0.9951	0.0
Solid content (C)	530.7	2	265.3	11.4	0.0006	43.8
A × B	12.5	4	3.1	0.134	0.9676	1.0
A × C	144.6	4	36.2	1.56	0.2283	11.9
B × C	8.7	4	2.2	0.0941	0.9831	0.7
A × B × C	17.3	8	2.2	0.0932	0.9990	1.4
Error/Residual	417.7	18	23.2			34.5
Total	1211.6	44				

Note: SS, sum of the squares; df, degree of freedom; MS, mean squares; *F*, *F* statistic for ANOVA, defined as the ratio of the sums of squares between treatments (MSB) and the error sums of squares (MSE).

Table 5 Y-hat model regression*

Source	Coeff.§	P (2 tails)
Constant	24.28	0.000
Processing temperature (A)	1.600	0.024
Holding time (B)	–0.033	0.961
Solid content (C)	–4.200	0.000
A × B	–0.375	0.624
A × C	–2.042	0.011
B × C	–0.542	0.480
A × B × C	–0.792	0.304
R^2	0.6128	
F	5.382	

Note: §Coefficient of the effect. *The proportion of orthogonality for each term all showed a tolerance of 1.00 which means orthogonal to each other and no multicollinearity.

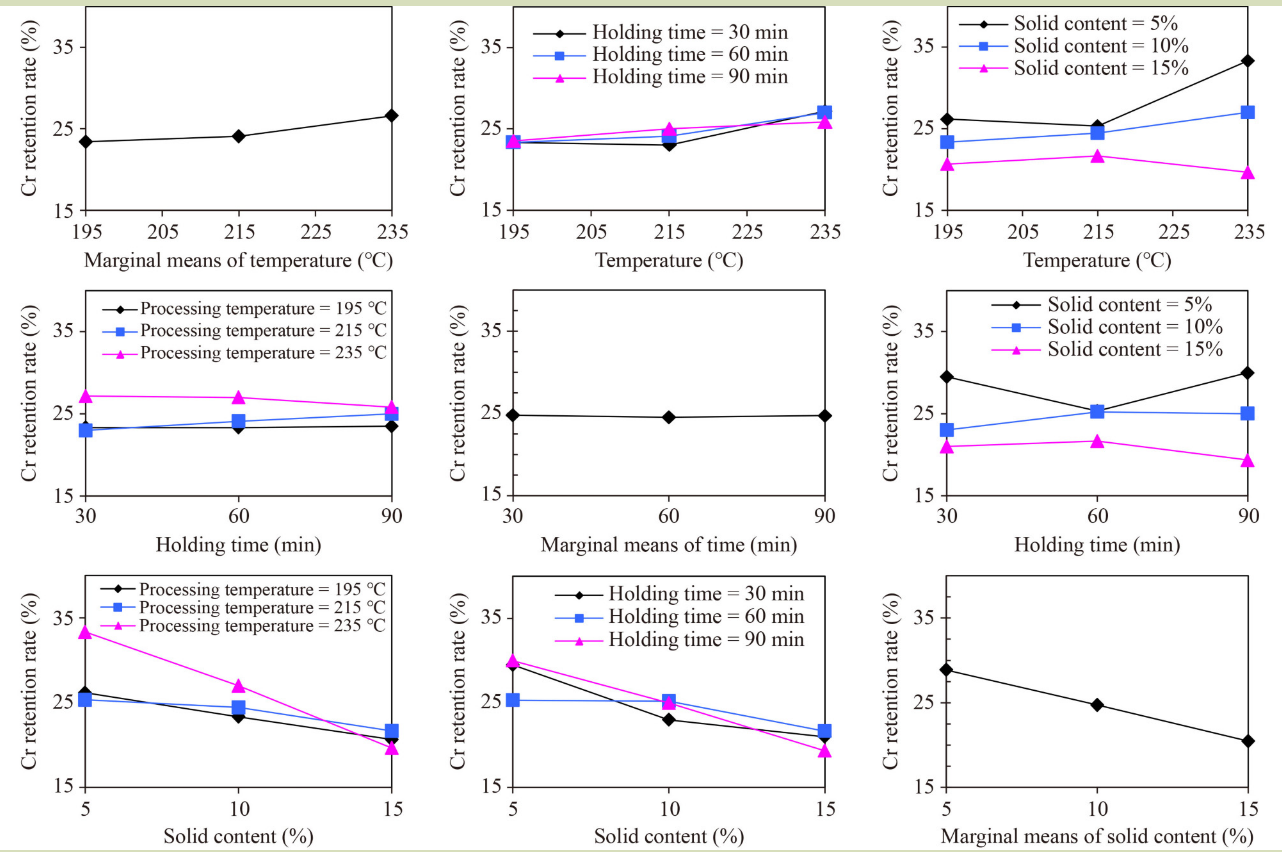


Fig. 4 Multiple plots of process parameters and interactions on Cr retention rates.

the three process parameters.

Further optimization analysis of the experimental results did not exhibit an overall optimal point for the minimization of Cr retention rate in the ranges of process parameters. Y-hat interaction plots in Fig. 5(a) show that the minimization point

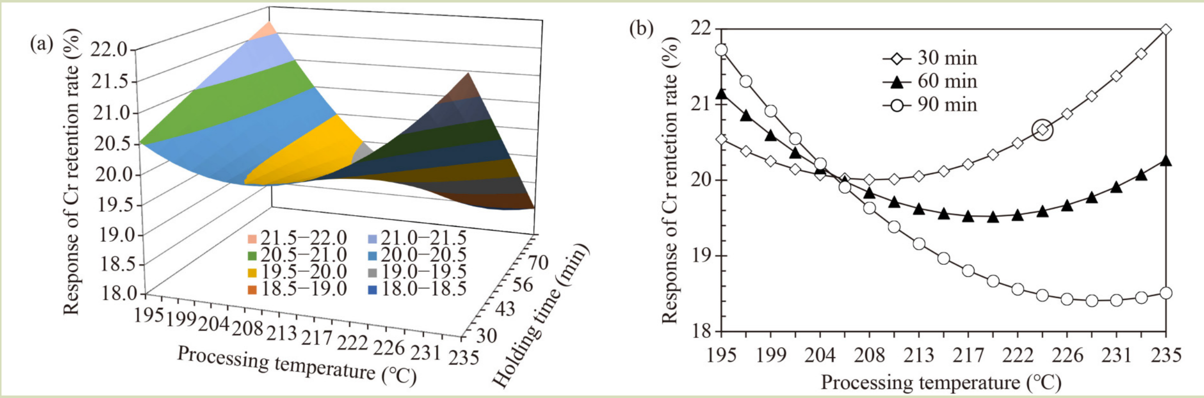


Fig. 5 Y-hat interaction plots showing the effects of (a) process parameters of processing temperature, holding time and solid content and (b) processing temperature and time at a constant solid content of 10%.

of Cr retention rate changes as the process parameters change. It was noticeable that, when the processing temperatures were in the range of 210–230 °C at a constant solid content of 10%, there were minimal points of Cr retention rate at the processing time of 30, 60 and 90 min (Fig. 5(b)). In the study of maximizing total phosphorus recovery rate from manure to hydrochar, the optimal processing conditions were 225 °C, 30 min and 10% of solid content[31]. Under that specific condition, the corresponding Cr retention was about 20.7% in hydrochar, as indicated by the red circle in Fig. 5(b).

4 CONCLUSIONS

This study revealed that HMs were retained in hydrochar in the range of 40%–100% after dairy manure was converted by hydrothermal carbonization. The processing temperature and solid content in the feed were the most influential process parameters that affected HM retention rate. Processing time did not significantly affect the HM retention. However, statistical analysis showed that there was no single optimal point to minimize HM retention in hydrochar.

Most detectable HMs in this study had higher concentrations in hydrochar (Table 6) than those initially in dairy manure (Table 2). Despite the higher concentrations, HMs in hydrochar were greatly below the US Environmental Protection Agency limits for land applications as biosolids, therefore, do not pose a serious concern when hydrochar is used as a phosphorus-enriched organic fertilizer and/or soil amendment for agricultural applications.

Table 6 Summary of heavy metals in hydrochar produced from dairy manure under various processing condition

Heavy metal	Concentration in hydrochar* ($mg \cdot kg^{-1}$)
Arsenic	< 40
Barium	44–60
Cadmium	< 0.8
Chromium	21–30
Copper	130–183
Lead	< 10
Mercury	nt
Molybdenum	< 10
Nickel	19–49
Selenium	nt
Zinc	373–473

Note: *Processing conditions were 180–255 °C of processing temperature, 30–120 min of processing time, and 2%–15% of solid content in manure feed. nt, not tested.

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Compliance with ethics guidelines

B. Brian He, Zheting Bi, and Lide Chen declare that they have no conflicts of interest or financial conflicts to disclose. This article does not contain any studies with human or animal subjects performed by any of the authors.

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