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# Dairy processing sludge feedstock-based biochars for the removal of phosphorus in discharge effluents

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## Abstract

Globally, the removal of phosphorus (P) in discharge effluents from industrial wastewater treatment is crucial to comply with discharge limits and to control eutrophication. The traditional practice involves the use of costly chemical coagulants to achieve required effluent quality. An alternative option is to utilize selected biochars derived from the pyrolysis of different dairy processing sludge feedstocks to capture P by replacing chemical use and thereby creating a circular economy. Sludge samples used to create biochar were of two types: a) bio-chemically treated mixed sludge and b) lime treated De-Areated Fat (DAF) sludge. Herein, biochar was added to synthetic and dairy wastewater and the overall efficacy of different biochars to remove P was determined along with biochar dosage, contact time, pH effect and P concentration levels. Results showed variable P removal across biochar type and composition. The biochars from mixed sludge showed 85−98% of P removal at dose between 10−50 g/L, whereas, those from DAF sludge removed >99% at 3 g/L. The P level was significantly reduced to <0.1 mg/L from dairy wastewater sample using DAF biochars. Water extractable P was found to be a factor that can be used to pre-screen biochar media for P attenuation capacity.

**Keywords:** Dairy processing sludge, Biochar, Phosphorus removal, Wastewater treatment

## 1. Introduction

Globally, an exponential growth in nutrient flows (e.g. nitrogen (N) and phosphorus (P)) through agricultural food systems has led to concerns about waste generation and water quality. This is particularly the case for the dairy processing industry, which is one of the main sources of industrial effluent in the European Union (EU) being the largest milk producer in the world (Finnegan *et al.*, 2017). Removal and reuse of P from dairy processing waste streams before discharge would aid the objectives of the EU Water Framework Directive i.e. good status for all waters. Also recycling this P as an organic fertilizer would benefit farmers, whilst creating a circular economy model. The removal of P from wastewaters can be achieved using chemical amendment, filtration through membrances or media (e.g. biochar, zeolite, activated carbon) or through biological means (Ashekuzzaman and Jiang, 2014). However, the current strategic requirement for sustainable P removal and recovery from industrial wastewaters demands alternative solution (Ashekuzzaman and Jiang, 2017). In the current study, biochar materials derived from the pyrolysis of different Dairy Processing Sludge (DPS) feedstocks were assessed to determine the efficacy in P removal from water samples. It can be considered that biochars are cheaply available from the energy recovery process of DPS and therefore, can be an alternative option for industry in capturing P using biochar media as a tertiary P sink to comply with stringent and strategic environmental policy regulated effluent discharge requirement.

## 2. Materials and Methods

### 2.1. Biochar

DPS samples from seven dairy processing plants (labelled as A to G) in Ireland were collected and converted to biochar through a pyrolysis process in a laboratory scale fixed bed reactor at the University of Limerick. The set-up was consisted of an electrically heated quartz reactor coupled with a water cooler and a receiving flask where the pyrolysis oil is collected. The outlet of this apparatus was connected to an extraction hood, where permanent gases were discharged. A batch of dried DPS (bench dried at ambient temperature) was placed in the reactor heated to 700°C, and kept at this temperature for 10 minutes during which the feedstock was pyrolysed. Then the heating jacket was turned off and the char was cooled down to room temperature while still in the reactor. The sludge samples were predominantly of two types: mixed sludge after bio-chemical treatment process (n=7, labelled as “M”) and lime treated De-Areated Fat (DAF) sludge (n=5, labelled as “D”). In this study, biochar samples are labelled as “XY-N” (e.g. AM-1, BM-2, BD-1, etc.) based on source and type, where X= Source (i.e. dairy processing plants), Y= Sludge type (i.e. M or D), N=Serial number. The proximate properties of the chars were analysed according to BS EN 14774-1: 2009 (moisture content), BS EN 14775: 2009 (ash content) and BS EN 15148: 2009 (volatile matter content). The elemental composition (C, H, N, S) was determined by a Vario EL cube elemental analyzer. The ash was digested and analyzed by ICP-OES spectrophotometer (Varian 710-ES), and the results for the individual metals are reported as their corresponding oxides. The major composition of biochar samples were dominated by the presence of $Al_2O_3$ (or $Fe_2O_3$), CaO, $SiO_2$ and $P_2O_5$ across DPS feedstock sources corresponding to a combined weight of these between 55−78% (Figure 1). The main source of Al, Fe and Ca oxides is associated with the use of chemicals (e.g. Al or Fe based coagulants and lime addition) for wastewater treatment at the individual processing plants. The prevalence of Al or Fe based oxides exists in mixed sludge feedstock based biochars (M1−M7) whereas D1−D5 contain more CaO. The use of these chemicals for reducing organic loads and nutrients from wastewaters results in a P enriched sludge ($P_2O_5$: 5−47%) due to the nature of P adsorption by Al, Fe and Ca- based (oxy)hydroxides. Among other components, the biochar composition includes $Na_2O$: 0.5−6.9%, MgO: 0.5−7.5%, $SO_3$: 0.2−8.2% and $K_2O$: 0.9−8.8%, depending on the source of DPS. These results indicate that the composition of biochars contrasts across different plant and sludge types, while some major components like $Al_2O_3$, CaO, $SiO_2$ and $P_2O_5$ dominate due to similar treatment practices. Heavy metal concentrations in biochars are significantly lower than those regulated by the EU in agricultural land for sludge recycling (Healy *et al.*, 2016) (Table 1).

### *2.2. Batch experiments*

The biochar samples were then sent to the Teagasc Environmental Research laboratory, where a series of batch experiments were conducted to assess P removal from both synthetic and dairy wastewater solutions as follows: a stock solution of $NaH_2PO_4$ dissolved in deionized water at 100 mg/L was made up and the working synthetic solutions with desired P concentration were made from the stock. The pH of working solutions was adjusted manually to the required values with diluted NaOH or HCl solutions. All the pH measurements were carried out with a pH meter (Cyberscan pH 11, Eutech Instruments) and the accuracy of pH reading was checked time to time using buffer solutions with pH of 4.0 and 7.0. P concentration was determined by Aquakem 600 Discrete Analyser at absorbance 880 nm following the ascorbic acid method (APHA, 2005). Dairy wastewater samples were collected in 4 L capacity plastic containers and stored at 4˚C for subsequent analysis of various water quality parameters. These parameters were determined according to the standard methods for the examination of waters and wastewater (APHA, 2005). The major water quality parameters in two selected samples were as follows: pH = 9.5 and 6.8, $BOD_5$ (mg/L) = 2558 and 1235, total P (mg/L) = 17.2 and 25.6, dissolved reactive P (DRP, mg/L) = 5.2 and 20.8, total N (mg/L) = 103.6 and 69.2, $NO_2$-N (mg/L) = 22.2 and 0.1, $NO_3$-N (mg/L) = 4.4 and 0.07, $NH_4$-N (mg/L) = 1.9 and 42.6,total carbon (TC, mg/L) = 2555 and 846.4, total organic carbon (TOC, mg/L) = 925 and 630. These two wastewater samples of contrasting characteristics were used to assess P removal capacity by the selected best performing biochar samples. For all biochars, batch experiments were conducted at room temperature in 50 mL screw-top polypropylene conical tubes by adding various doses of adsorbent materials into 25 mL of synthetic solution with initial total P concentration of 10 mg/L and pH ~7. The mixing of adsorbents and synthetic solution was performed by using an end-to-end shaker at 20 rpm for 24 h. After shaking, the suspension was immediately centrifuged for phase separation and the supernatant pH was measured. Finally, the supernatant was filtered (0.45μm Whatman filter disc), and analysed to determine the residual P concentration. The equilibrium contact time of optimal adsorption was determined at a selected dose for variable time intervals i.e. from 0.5 to 6 h. The P sorption study was performed under different initial P concentrations (5−50 mg/l) and at various initial pH levels (3−10) to determine the adsorption isotherms and the effect of pH, respectively. In both of these cases, pre-determined contact time and adsorbent dose were applied keeping other procedures same as mentioned above. The results are presented as the average of duplicate trials, and the reproducibility of the results were varied within the standard deviation <±5%. The adsorption capacity (Qe, mg/g) or quantity of P adsorbed by the sorptive media, and removal rate (R) of P were calculated from the following relations:

$$Q_e = \frac{(C_o - C_e)\cdot V}{m}, \qquad R\ (\%) = 100 \times \frac{C_o - C_e}{C_0}$$

where $C_o$ is the initial concentration of the P (mg/L), $C_e$ is the equilibrium or residual P concentration (mg/L), $V$ is the volume of the solution (L) and $m$ is the mass of adsorbent (g). The concentration of various elements and metals in the aqueous phase was determined using ICP-OES (Agilent 5100 SVDV). Water extractable P (WEP) was determined according to Kleinman *et al.* (2007) for all biochar samples to assess P desorption from the compositional $P_2O_5$ fraction of these samples.

## 3. Results and Discussion

### *3.1. Study with synthetic P solution*

Biochar samples (n=12) were pre-screened based on their P sorption performance from synthetic solution ([P] = 10 mg/L, pH~7.0). It was observed that 6 samples had increasing P removal capacity at increasing doses up to a certain dosage across the samples. Where the P removal trend flattened out an optimal dosage for each biochar was selected. The results showed that biochar samples pyrolysed from DAF sludge (i.e. BD-1, CD-2) removed >99% of P at comparatively lower dosage (3 g/L) than those from mixed sludge (i.e. AM-1, BM-2, CM-3) (Figure 2). The later char samples showed 85−98% P removal with a dosage between 10−50 g/L. The remaining 6 samples (DM-4, EM-5, GM-7, DD-3, ED-4 and GD-5) did not exhibit P sorption properties when added to synthetic solution, with desorption increasing the P concentrations in the supernatant. The selected char samples (n=5) were studied as a function of contact time to identify equilibrium time at which the optimal level of P adsorption is achieved at selected dose. It was found that contact time between 3−4 h was sufficient across the adsorbent samples, resulting 90−99% of P removal from 10 mg-P/L (Figure 2). The effect of different initial pH values ranging from 3 to 10 on the P removal performance by the selected materials was assessed and the results are shown in Figure 3. The removal of P was not affected between pH range 3−7 for samples AM-1, BD-1 and CD-2. With further increase in pH up to 10.0, the removal rate was decreased from 97−99% to 89−97%, showing higher decrease rate for CD-2. The sample BM-2 showed highest P removal at pH of 3.0 following a decreasing trend with pH increase

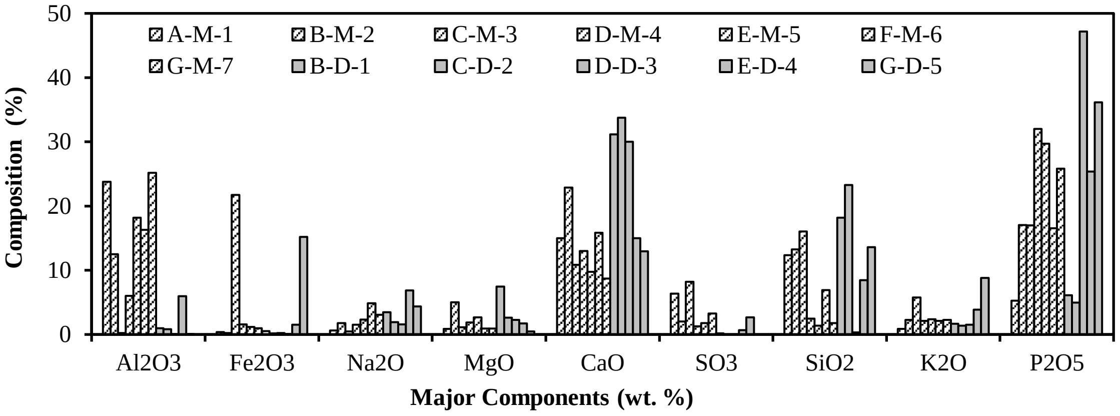


**Figure 1** Major elemental composition of biochar samples. Vertical hatching and shaded bars represent composition in biochars prepared respectively from mixed (M1-M7) and DAF (D1-D5) sludge.

**Table 1.** Heavy metal levels (mg $Kg^{-1}$) in biochar samples and their upper limit values for use in agriculture.

| Biochars | Pb | Cd | Cu | Ni | Hg | Zn | Cr | Sb | Se |
|---|---|---|---|---|---|---|---|---|---|
| M 1−7 | 1.5−11 | 1.2−5 | 24−152 | 12−27 | nd | 67−393 | 28− 42 | nd−12 | nd−36 |
| D 1−5 | 6−9 | 1.2−3 | 15−48 | 5−44 | nd | 12−663 | 5−87 | nd−10 | nd−18 |
| EU limit[1] | 1200 | 40 | 1750 | 400 | 25 | 4000 | ns |  | 100 |

[1] EU regulatory limit values (Healy *et al.*, 2016); nd: not detected; ns: no standard

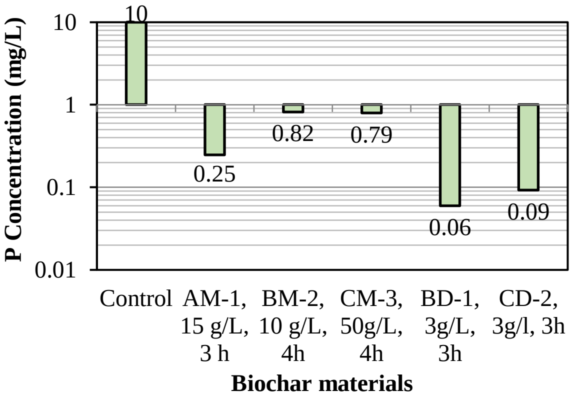


**Figure 2** Adsorption of phosphate on selected biochar materials at equilibrium dose and contact time.

between 4−10, except at pH of 7. Another sample CM-3 showed increasing trend of P removal from 88% to 92% with pH increase from 3 to 9 followed by a reduced P removal (88%) at pH of 10.In general, the decrease in P sorption by adsorptive media at higher pH values (e.g. >7.0) is associated with two facts: (i) higher pH causes increasing competition for adsorption sites between $OH^{-}$groups and phosphate species (e.g. mainly $HPO_4^{2-}$ at pH>7.5) and (ii) a higher pH can cause the adsorbent surface to carry more negative charges and thus would enhance repulsive interaction between the adsorbent surface and the anions in solution (Ashekuzzaman and Jiang, 2014). The equilibrium pH was observed to be raised to between 9.7−11.0 for most of the samples after sorption at initial solution pH range 3−7 with no significant changes in P removal rate. This means ligand exchange interaction between hydroxide ions ($OH^{-}$) of the char surface and anionic phosphate species played an important role in P removal process. Moreover, the high level of CaO content in the char samples (Table 1) can be associated with Ca-P precipitation at the observed equilibrium pH range.

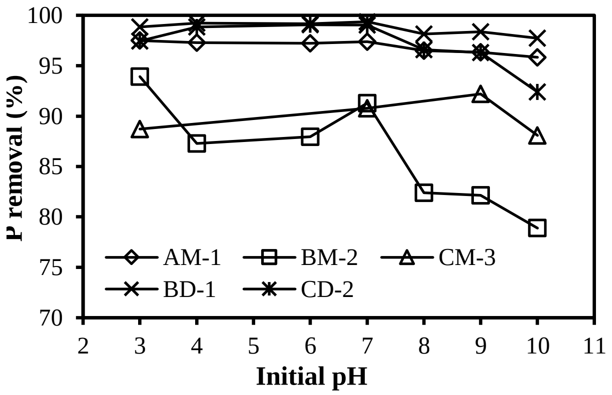


**Figure 3** Effect of pH on the uptake of phosphate.

The results of the effect of initial P concentration showed that the residual P concentration was acieved up to 0.06 mg/L against start P levels between 5−10 mg/L in the synthetic solution. With further increase of initial P concentration, the residual concentration was observed to be increased i.e. P removal decreased due to the lack of available active sites that can uptake increased phosphate species at fixed adsorbent dosage. This phenomenon was also observed in previous studies (Jiang and Ashekuzzaman, 2015). The adsorption data were fitted to both Langmuir and Freundlich isotherm model relationships and values of isotherm constants are shown in Table 2. The adsorption isotherms can be better predicted by the Freundlich model for most of the samples (except

AM-1) as observed from the greater or approximately closer correlation coefficients ($R^2$) to those in Langmuir fitting. In Freundlich model, larger $K_f$ indicates greater overall adsorption capacity, which is in correspondence with the estimated maximum P sorption capacity as per Langmuir model following the order BD-1>CD-2>AM-1>BM-2 (Table 2). This indicates biochar samples from DAF sludge have the higher P sorption capacity (6.4−7.3 mg/g) than those from mixed sludge (3.2−4.8 mg/g), and these sorption capacities are comparable or higher to those of other low-cost adsorbents (e.g. fly ash, blast furnace slag, modified activated carbon) (Ashekuzzaman and Jiang, 2014).

**Table 2.** Isotherm model constants for phosphate adsorption on adsorbent samples.

| Isotherms | Adsorbents | | | |
|---|---|---|---|---|
| | AM-1 | BM-2 | BD-1 | CD-2 |
| ***Langmuir isotherm*** $(\frac{1}{q_e} = \frac{1}{q_o b C_e} + \frac{1}{q_o})$ | | | | |
| $q_o$ (mg/g) | 4.8 | 3.2 | 7.3 | 6.4 |
| b (L/mg) | 0.85 | 0.25 | 6.74 | 5.95 |
| $R^2$ | 0.929 | 0.752 | 0.759 | 0.882 |
| ***Freundlich isotherm*** ($\log q_e = \log K_f + \frac{1}{n} \log C_e$) | | | | |
| $K_f$ | 1.66 | 0.72 | 4.32 | 3.68 |
| n | 2.01 | 1.93 | 4.49 | 5.11 |
| $R^2$ | 0.780 | 0.889 | 0.869 | 0.869 |

$q_o$ = maximum adsorption capacity (mg/g), b = adsorption equilibrium constant (L/mg), $q_e$ = adsorption capacity at equilibrium (mg/g), $C_e$ = equilibrium adsorbate concentration (mg/L), $K_f$ and n are the Freundlich isotherm constants.

Considering the elemental composition of char samples (showed in Table 1), the elemental retention capacity of these were assessed while using for P sorption from synthetic solution ([P]=10 mg/l, pH~7.0, T = 24 h). The results showed that most of the compositional elements were retained (<5% release), except the release of Na (8−85%) and K (1.5−37%) from some of the samples (Figure 4). In this case, BD-1 and CD-2 samples showed the lowest release of any element (<1.5%) including Na and K. The release of heavy metals (Pb, Cd, Cu, Ni, Zn, Cr, Mn) were quite negligible and the level concentrations were between 0.24−11.5 µg/L where detected.

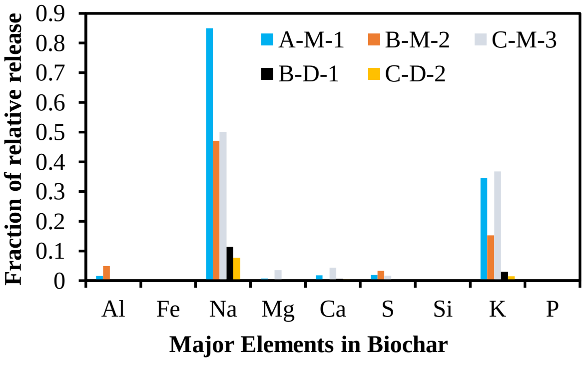


**Figure 4** Relative releases of different elements from biochar samples during P sorption.

The data of WEP for all biochar samples were fitted against the respective residual P concentrations observed at selected optimal dosage, where a significant correlation ($R^2$=0.97, significance F <<0.05) was observed (**Figure 5**). Accordingly, samples with WEP <1 mg/L showed between 85−99% of P removal from synthetic solution, while those with WEP between 1.3−8.9 mg/L having poor P removal capacity i.e. residual P concentrations were close to 10 mg/L. This means that WEP can be used as a factor to pre-screen sorption media for P attenuation, particularly media containing P component in the composition.

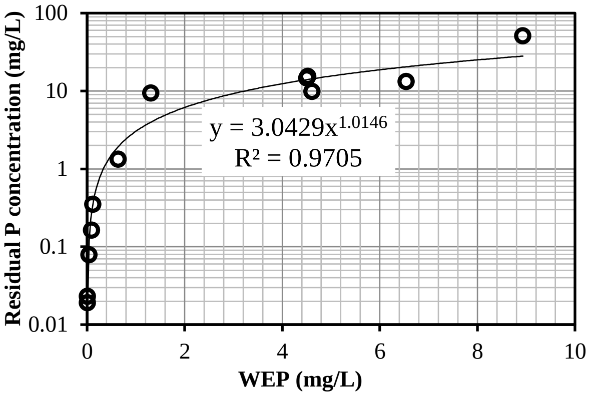
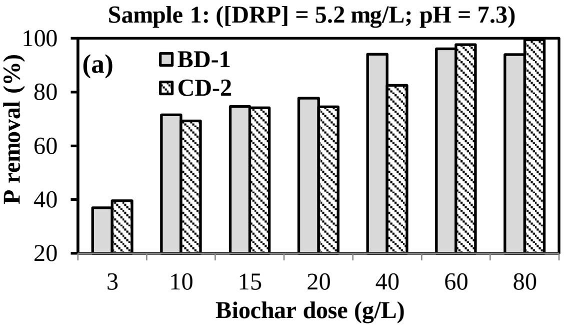


**Figure 5** The relationship between WEP in biochar samples and the residual concentration of P in sorption test.

*3.2. Dairy wastewater sample*

The best performed biochar samples BD-1 and CD-2 were used to determine the level of DRP that can be removed from two dairy wastewater samples of contrasting characteristics. The results demonstrated 96−99.8% of DRP removal from both wastewater samples at dosage of 60 and 80 g/L by the both char samples (**Figure 6**). This indicates that dairy processing wastewaters having DRP concentration of 5−21 mg/L can be treated with selected biochar adsorbents to reduce the P level down to <0.1 mg/L in the finally treated effluent.



## 4. Conclusions

Biochars can be derived from the pyrolysis of two dairy processing sludge streams. The first originates from a mixed stream and showed 85−98% P removal at dose between 10−50 g/L. The second originates from a DAF stream and removed >99% of P at dose of 3 g/L. The equilibrium contact time to achieve the optimal level of P adsorption was between 3−4 h. In general, P removal was better when the solution had initial pH range between 3−7 than pH>7. The adsorption data fitted well with the

Freundlich isotherm model and accordingly the P removal capacity of biochars can be ranked as BD-1>CD-2>AM-1>BM-2, indicating that DAF biochars have the higher P sorption capacity (6.4−7.3 mg/g) than those from mixed sludge (3.2−4.8 mg/g). The results revealed that water extractible P can be used as a quick pre-screening test for selecting biochars as P attenuation media. Overall, this study demonstrates a potential for further investigation of using selected DPS feedstock based biochar in P attenuation at pilot-scale and also to identify other physicochemical mechanisms of P sorption-desortion process with bochars.

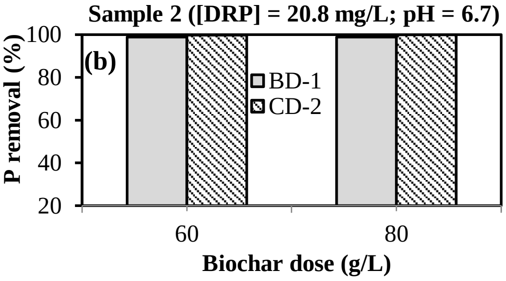


**Figure 6** Removal of DRP from wastewater samples with different level of P concentrations using selected biochars.

## Acknowledgement

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