

Utilising highly characterised peats to remove cadmium from aqueous solutions

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SUMMARY

This research investigated the biosorption of cadmium (Cd) from aqueous solutions by six highly characterised peats. Samples of the peats were tested both in unaltered condition and after treatment with hydrochloric acid (HCl) to free up any occupied exchange sites. Other factors tested were sample dose, contact time, mixing temperature, and the concentration and pH of the Cd solution. Desorption studies were also performed, and tests were done to determine whether the peats could be re-used for Cd biosorption. The results indicate that all six peats biosorb Cd from aqueous solution well (36–100 % removal) and that their Cd removal capacities are affected by the various factors that were manipulated. The three factors that had the greatest effects on the Cd removal capacities of the peats were sample dose and the concentration and pH of the Cd solution. The percentage of Cd removed increased as the sample dose increased (16–31 % increase) and as the pH of the Cd solution increased (16–57 % increase). As the concentration of the Cd solution increased, the percentage of Cd removed increased slightly for two of the six peats (1–2 % increase) and decreased for three peats (19–23 % decrease). As the mixing temperature increased, the percentage of Cd removed increased slightly for three of the peats (1–12 % increase) and decreased slightly for the other three (1–5 % decrease). The desorption results showed a 34–71 % Cd recovery rate. Re-used peats were also highly effective at removing Cd, whether or not they had gone through desorption. Two of the six peats were slightly better at Cd removal after treatment with HCl (4–7 % better than untreated peats), while the other four peats worked better in their unaltered states (3–18 % better). As all of the peat types tested can be repeatedly re-used for additional Cd biosorption cycles, their disposal should not create a hazardous waste problem. On the other hand, using peat for any industrial purpose is increasingly disfavoured nowadays, for sustainability reasons. Thus, the results of this study might be used to identify and/or develop materials with properties similar to those of the most effective peats (i.e. artificial peats) for use as biosorbents of Cd. These materials could be agricultural waste products such as soybean or rice hulls, constructed wetlands with living plants similar to those found in the tested peats, or possibly biochar of these living plants.

KEY WORDS: biosorption, cost-effective, environmentally friendly, heavy metals, remediation

INTRODUCTION

One of the major sources of heavy metal water pollution is the industrial wastewater effluent produced by industries including metal plating, mining, oil refining, rubber processing, tanning and chemical manufacturing (Meena *et al.* 2008). The metals lead, cadmium, chromium (VI) and mercury have some of the highest toxicities. Traditional removal techniques such as ion exchange and precipitation, reverse osmosis, electrodialysis, lime coagulation, and adsorption using activated carbon and lime ash may not completely remove heavy metal waste, and can generate toxic sludge. These methods are also costly and have high energy input requirements (Krishnani *et al.* 2008). Thus, there is a

need for new heavy metal remediation technologies that are cost-effective and environmentally friendly.

Biosorption is a fairly new technique that has been presented as both effective and inexpensive in comparison to chemical and physical technologies (Krishnani *et al.* 2008). Biosorption is the binding of metal ions and radionuclides onto the cellular structures of biological materials, including their ligands and functional groups. Materials that are lignocellulosic (containing cellulose, hemicellulose and lignin) have high adsorption properties due to their ion exchange capabilities and can, accordingly, be used effectively as biosorbent materials (Krishnani *et al.* 2008). Various biosorbent materials have been found to work well at removing heavy metals from aqueous solutions. It has also been

shown that biosorbent materials can be regenerated for re-use, and adsorbed metal ions can possibly be recovered from the biosorbent material (Volesky 2007). In addition, biosorbent materials are cost effective, efficient, do not require much energy input, and do not produce toxic sludge. Their efficacy fluctuates when various factors such as pH, metal concentration, adsorbent dose, particle size and contact time are modified.

Peat is an abundant and inexpensive naturally occurring organic-rich material derived from plants that several studies have shown is effective at removing heavy metals from aqueous solutions. Four good reviews of the literature up to 2003 are provided by McLellan & Rock (1986), Bailey *et al.* (1999), Brown *et al.* (2000) and Babel & Kurniawan (2003), and additional relevant references include Chen *et al.* (2001). Several studies including our own (Cohen & Stack 1995, Rizzuti *et al.* 1996, Stack *et al.* 1996, Rizzuti *et al.* 2003, Rizzuti *et al.* 2015, Rizzuti *et al.* 2017) have shown that the amounts and rates of metal extraction can differ greatly between one type of peat and another. This is because different peat types can vary widely in their botanical composition as well as in their chemical and physical properties. A few studies have looked at the Cd removal capacity of peat (Li & Champagne 2009, Chaney & Hundemann 1979, Coupal & Lalancette 1976). In these studies, the Cd removal capacities of moss (e.g. *Sphagnum*) peats (only) were tested.

The United States of America (USA) Environmental Protection Agency (EPA) has set the goal for maximum Cd contaminant level in drinking water at 5 ppb ($5 \mu\text{g L}^{-1}$). The study reported here was commissioned by the Department of Energy (DOE) to develop cost effective and environmentally friendly Cd remediation techniques, specifically in the context of Cd being discharged into watercourses at various DOE sites in the USA. The purpose of this study was to determine the capacities of six different highly characterised peat types for biosorption of Cd from aqueous solutions at typical concentrations for waterborne Cd observed at various DOE sites (within the range $0.1\text{--}30 \text{ mg L}^{-1}$).

MATERIALS AND METHODS

Materials

The peats were obtained from the peat sample bank at Claflin University (Cohen *et al.* 1991). Six different peat types were chosen to represent a wide range of peat-forming environments and chemical and physical properties. The peat types were the same

as those previously tested as biosorbents for mercury and hexavalent chromium (Rizzuti *et al.* 2015, 2017), but for reader convenience the Table describing their characteristics is repeated as an Appendix to this article.

The Cd solutions were prepared by diluting a 100 mg L^{-1} stock solution (in 5 % nitric acid) to the desired concentrations in ppm (mg L^{-1}) using ASTM Type II deionised water. The concentration of the initial working standard was 5 mg L^{-1} .

All of the glassware used in this research was soaked in 10 % nitric acid for two hours and rinsed thoroughly with Type II deionised water. All sample tubes were soaked overnight in a 40 % HCl solution and rinsed with deionised water.

Mixing procedure

For the 'standard' procedure, 0.5 g of peat was weighed out, placed in a 125 ml flask, and 50 ml of 5 mg L^{-1} Cd solution was added. The flask was then placed on a shaker (Thermo Scientific MaxQ 2000) at $\sim 175 \text{ rpm}$ to mix for 24 hours at $24 \pm 1 \text{ }^\circ\text{C}$. In order to test the effects of different factors on the removal of Cd, we varied the quantity of peat, the concentration of the Cd solution, the mixing time, and other factors. Details of the various treatments that were applied are given below. All assays were conducted in triplicate and the results showed a relative standard deviation of less than 2 %.

Sample dose

To investigate the effect of sample dose, 0.125, 0.25 or 0.5 g of peat was mixed with 50 ml of 5 mg L^{-1} (pH 3.0) Cd solution for 24 hours.

Contact time

To study the effect of contact time, 0.5 g of each peat type was mixed with 50 ml of 5 mg L^{-1} (pH 3.0) Cd solution for 2, 24 or 48 hours.

Mixing temperature

To determine the effect of mixing temperature, 0.5 g of peat was mixed with 50 ml of 5 mg L^{-1} (pH 3.0) Cd solution for 24 hours in a temperature-controlled shaker set at room temperature ($24 \pm 1 \text{ }^\circ\text{C}$), $30 \text{ }^\circ\text{C}$, $35 \text{ }^\circ\text{C}$ or $40 \text{ }^\circ\text{C}$.

Cd solution concentration

To investigate the effect of Cd solution concentration, 0.5 g of each peat type was mixed with 50 ml of 1, 5, or 10 mg L^{-1} (pH 3.0) Cd solution for 24 hours. These (low) concentrations were chosen to represent the waterborne Cd concentrations found in watercourses surrounding various DOE sites.

pH of Cd solution

To test the effect of varying the pH of the Cd solution, 0.5 g of each peat type was mixed with 50 ml of 5 mg L⁻¹ Cd solution at different pHs in the range 2–10 (increment unity; Thermo Scientific Orion 2 Star pH benchtop meter) for 24 hours. This was achieved by adjusting the pH of the working Cd solution above or below that of the initial working standard solution (3.0±0.1) using a 0.05N solution of sodium hydroxide and 0.01N nitric acid.

HCl treatment

The purpose of the HCl treatment was to remove metal ions attached to the peat sample and, hence, free up exchange sites to bond with Cd ions. Each sample was mixed with 10 % HCl for one hour. This step was repeated with fresh HCl for another hour. The sample was then washed with deionised water until a pH of approximately 6 was reached. Next, 0.5 g of the HCl-treated peat sample was mixed with 50 ml of a 5 mg L⁻¹ (pH 3.0) Cd solution for 24 hours.

Desorption of Cd

To determine whether the removed Cd could be recovered and recycled, peat samples that had been used for biosorption of Cd were tested to determine the amount of Cd that could be desorbed from them afterwards. Peat which had already been used once (0.5 g of sample mixed for 24 hours with a 5 mg L⁻¹ Cd solution at pH 3.0) was mixed with 100 ml of 10 % HCl for two hours.

Re-using samples for biosorption of Cd

Peat samples that had been used for biosorption of Cd were also tested to determine whether they could be re-used for this purpose and whether desorbing the Cd from the peat would improve its effectiveness when re-used. Samples were tested (with and without going through desorption) for their Cd removal capacities after being used once. Peat that had already been used once for biosorption of Cd (24 hours with 5 mg L⁻¹ Cd solution at pH 3.0) was mixed with 50 ml of fresh 5 mg L⁻¹ Cd solution (pH 3.0) for 24 hours.

Measurement of cadmium remediation

After shaking, the Cd solutions were centrifuged (Eppendorf 5810 R) for 15 minutes to separate any remaining peat, vacuum filtered through 0.45 µm nylon filters, then analysed for Cd concentration. The Cd concentration was measured using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-MS) (Profile Plus, Teledyne Leeman Labs, NH). Before each analysis session, calibration standards (1, 5, 10, 20 and 30 mg L⁻¹) were freshly

prepared from the 100 mg L⁻¹ Cd stock solution and used to establish a standard calibration curve.

RESULTS

The results (Table 1) demonstrate that all six peat types worked well at biosorbing Cd from aqueous solutions (36–100 % removal). In general, all of the manipulations tested had at least some effect on the Cd removal capacities of the peats. The largest effects were obtained by manipulating sample dose, as well as the concentration and pH of the Cd solution.

Effect of sample dose

Mixing with a small amount (0.125 g) of all peat types resulted in a slight to substantial (36–81 %) removal of Cd from the aqueous solutions. As the sample dose was increased from 0.125 g to 0.5 g, the percentage of Cd removed increased greatly (16–31 % increase). The greatest increase (31 %) was observed for LN peat.

Effect of contact time

Maximum Cd removal capacity was reached within a contact time of 2 hours for one of the six peat types (LN), and otherwise required up to 24 hours (four peat types: MS, ON, OT, RH) or 48 hours (one type: LS). For all of the peats, increasing contact time from 2 hours to 48 hours did not significantly affect their Cd removal capacities (0–2 % increase). The Cd removal capacity of one peat type (LN) decreased by 1 % after 48 hours. The kinetic curves (Figure 1) show that the removal of Cd by all peat types predominantly occurred during the first two hours of contact, which were followed by 46 hours of equilibrium or near-equilibrium conditions.

Effect of mixing temperature

As the mixing temperature was increased from 24 °C to 40 °C, the percentage of Cd removed decreased slightly (by 1–5 %) for three of the six peats. The greatest decrease (5 %) was for MS peat. For two of the six peats there was a slight (1–2 %) increase, while for ON peat the increase was 12 %.

Effect of cadmium solution concentration

Increasing the Cd solution concentration from 1 mg L⁻¹ to 10 mg L⁻¹ reduced Cd removal capacity for three of the six peats (87 % to 64 % for MS; 86 % to 67 % for ON; 87 % to 65 % for OT). The greatest decrease (23 %) was for MS peat. One peat type (LN) showed no change, while the Cd removal capacities of the other two peats increased slightly (1–2 %).

Table 1. Percent cadmium biosorption by each of the six peat types with variation of the factors that were manipulated.

| Factor | Value | Peat type | | | | | |
|--|--------------------|-----------|----|-----|----|-----|-----|
| | | MS | ON | LS | OT | RH | LN |
| Sample dose (g) | 0.125 | 41 | 36 | 81 | 40 | 73 | 65 |
| | 0.250 | 47 | 46 | 96 | 47 | 92 | 94 |
| | 0.50 | 68 | 66 | 97 | 66 | 97 | 96 |
| Contact time (hr) | 2 | 58 | 64 | 97 | 62 | 96 | 98 |
| | 24 | 68 | 66 | 97 | 66 | 97 | 96 |
| | 48 | 60 | 66 | 98 | 62 | 97 | 97 |
| Mixing temperature (°C) | 24 | 68 | 66 | 97 | 66 | 97 | 96 |
| | 30 | 61 | 68 | 98 | 62 | 96 | 96 |
| | 35 | 58 | 70 | 99 | 60 | 96 | 97 |
| | 40 | 63 | 78 | 98 | 62 | 96 | 98 |
| Cadmium solution concentration (mg L ⁻¹) | 1 | 87 | 86 | 98 | 87 | 93 | 96 |
| | 5 | 68 | 66 | 97 | 66 | 97 | 96 |
| | 10 | 64 | 67 | 99 | 65 | 95 | 96 |
| pH | 2 | 41 | 44 | 84 | 43 | 77 | 57 |
| | 3 | 68 | 66 | 97 | 66 | 97 | 96 |
| | 4 | 75 | 88 | 99 | 77 | 98 | 98 |
| | 5 | 77 | 86 | 99 | 76 | 100 | 99 |
| | 6 | 75 | 96 | 99 | 82 | 98 | 99 |
| | 7 | 94 | 98 | 99 | 95 | 99 | 100 |
| | 8 | 97 | 99 | 100 | 97 | 99 | 99 |
| | 9 | 93 | 98 | 100 | 98 | 99 | 99 |
| | 10 | 98 | 98 | 100 | 98 | 99 | 100 |
| | HCl treatment | without | 68 | 66 | 97 | 66 | 97 |
| with | | 65 | 70 | 90 | 73 | 79 | 84 |
| Re-use | first use | 68 | 66 | 97 | 66 | 97 | 96 |
| | after desorption | 66 | 68 | 87 | 70 | 76 | 86 |
| | without desorption | 43 | 47 | 98 | 45 | 97 | 96 |

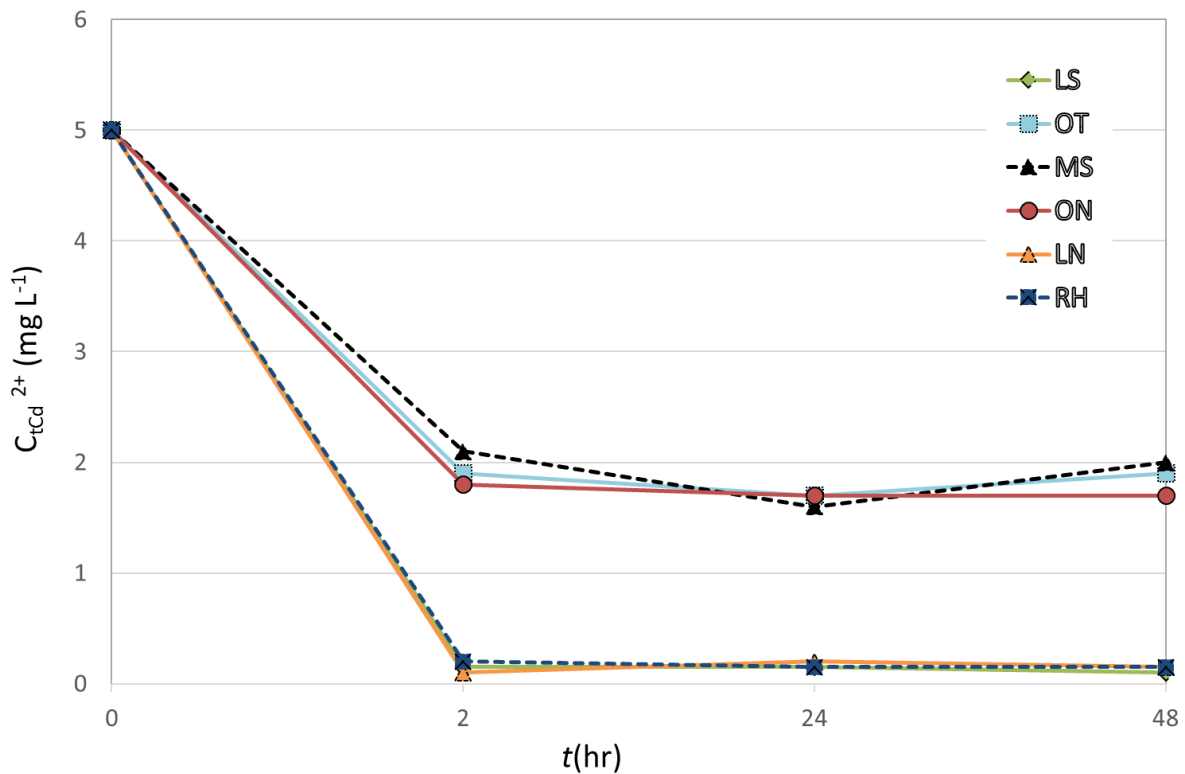


Figure 1. Kinetic curves showing change in the concentration of Cd in solution ($C_{tCd^{2+}}$, $mg L^{-1}$) with time (t , hr) for a $C_{0Cd^{2+}}$ of $5 mg L^{-1}$, for each of the six peat types tested. Note that the scale on the horizontal axis is not linear.

Effect of pH of cadmium solutions

As the pH of the Cd solution was increased from 2 to 10, the Cd removal capacities of all six peat types increased significantly (by 16–57 %). The largest change in percentage of Cd removed occurred with MS peat (41 % at pH 2 to 98 % at pH 10).

Effect of HCl treatment

Treating with HCl reduced the ability of four of the six peats to remove Cd from solution (3–18 % decrease) and slightly increased the Cd removal capacities of the other two peats (4–7 % increase). The greatest effect was observed for RH peat, whose Cd removal capacity was 97 % in unaltered condition and 79 % after HCl treatment.

Desorption of cadmium

The desorption results indicate that it may be possible to recover and recycle some to most of the removed Cd from the peat samples. The MS peat had 36 % of the Cd desorbed, ON had 49 % desorption, LS had 69 % desorption, RH had 71 % desorption, LN had 66 % desorption and OT had 34 % desorption.

Re-use of samples for biosorption

All six peats worked well when re-used for additional

Cd biosorption cycles. Three of them performed better when re-used after going through desorption than without desorption (MS 23 % better, ON 21 % better, OT 25 % better), while the other three worked better when re-used without going through desorption (LS 11 % better, RH 21 % better, LN 10 % better). These results indicate that all six peat types can be re-used for Cd biosorption, whether or not they go through desorption in between the two biosorption cycles.

In order to investigate which physical or chemical characteristics of the six tested peat types might be related to their Cd removal capacities, the Cd removal results (0.5 g of each peat type mixed with 50 ml of $5 mg L^{-1}$ Cd solution at pH 3.0 for 24 hours) were plotted against key characteristics of the peats. The Cd removal results showed possible relationships ($R^2 > 0.5$) with only five of the key peat characteristics, namely: calcium content, magnesium content, sulphur content, total aldehydes content and the quotient (humic acids content ÷ fulvic acids content). In general, as the calcium, magnesium, and sulphur contents of the peat types increased, their Cd removal capacities also increased (Figures 2a–2c). In contrast, as the total aldehydes content and the (humic acids content ÷ fulvic acids content) quotient

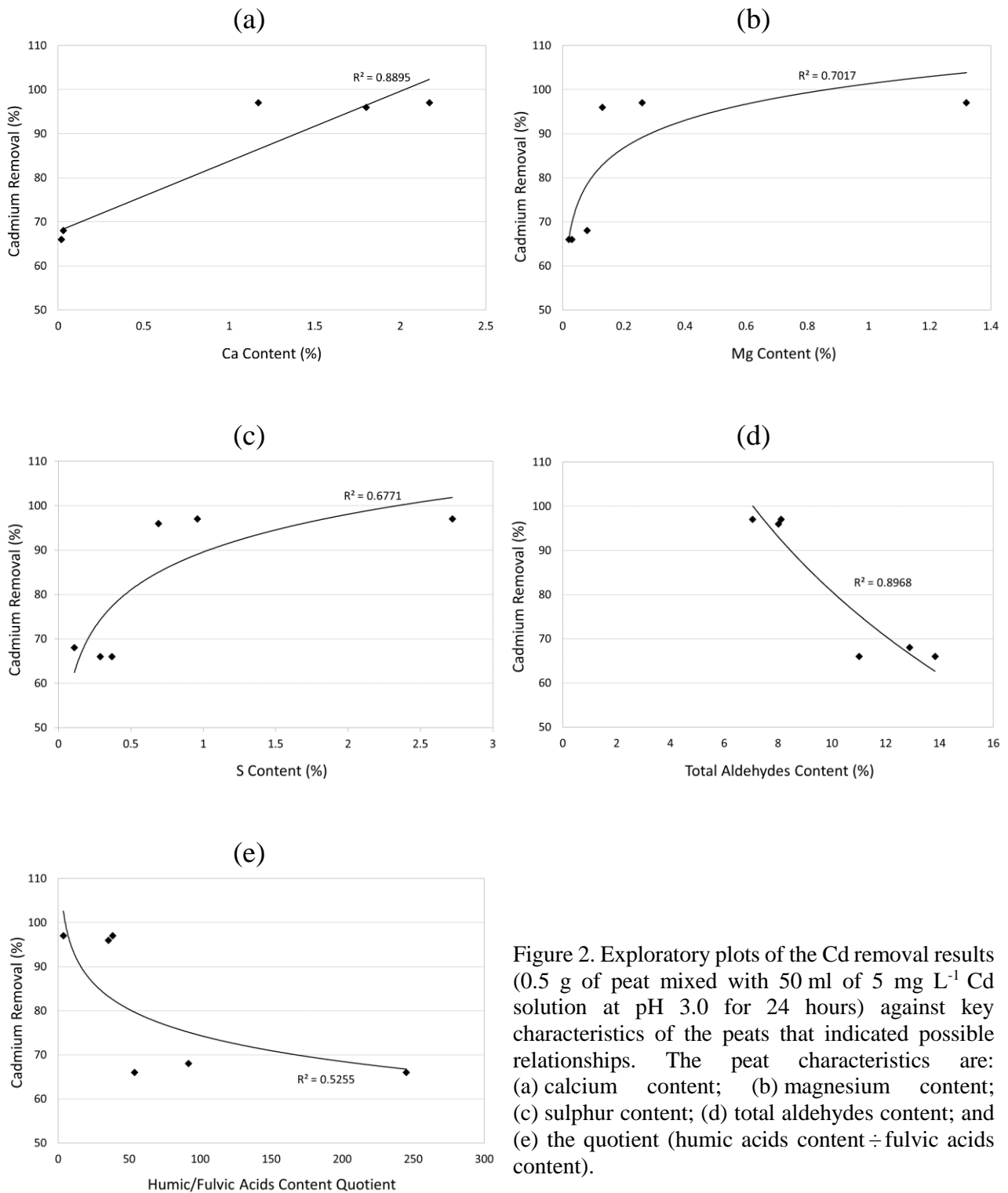


Figure 2. Exploratory plots of the Cd removal results (0.5 g of peat mixed with 50 ml of 5 mg L⁻¹ Cd solution at pH 3.0 for 24 hours) against key characteristics of the peats that indicated possible relationships. The peat characteristics are: (a) calcium content; (b) magnesium content; (c) sulphur content; (d) total aldehydes content; and (e) the quotient (humic acids content ÷ fulvic acids content).

of the peat types increased, their Cd removal capacities decreased (Figures 2d–2e). It is emphasised that this is an initial exploration of the data to obtain a first indication of which properties of the peat may influence the sorption process. Further assays utilising several more peat types would be needed to confirm the relationships suggested by this analysis.

DISCUSSION

Peat has a unique chemical and physical makeup and possesses a variety and high number of polar functional groups. The most likely reason that all of the six peat types trialled here worked well at removing Cd from aqueous solutions is the high

affinity of their functional groups (see Appendix) for Cd. These polar functional groups appear to be capable of removing large amounts of Cd ions from aqueous solutions.

Manipulating various factors affected the Cd removal capacities of the peats. Of the factors whose effects were tested here, sample dose, the concentration of the Cd solution and its pH had the greatest impact on Cd removal capacities. Both the surface charge of the adsorbent material and the level of ionisation and speciation of the metal are affected by pH (Tekler *et al.* 1999). Previous studies have found the optimal pH levels for metal sorption by biomass to be 5–6 and that both highly acidic and highly alkaline environments significantly reduce sorption capacity (Krishnani *et al.* 2008, Meena *et al.* 2008). The results of this study indicate that the optimal pH level for Cd removal varies amongst the six peat types tested. Three types removed 96–100 % of the Cd at pH values of 3–10, two types removed 93–98 % at pH 7–10, while one type removed 96–99 % at pH 6–10. All of the peat types tested removed the smallest amount of Cd at pH 2. The optimal pH level for Cd removal was 5 for RH peat, 7 and 10 for LN peat, 8 for ON peat, 8–10 for LS peat, 9–10 for OT peat, and 10 for MS peat. An explanation for this could be that, at lower pH, the biosorbent is positively charged due to protonation so that positively charged Cd cations (Cd^{2+}) are not attracted to it (Gupta *et al.* 2010). As the pH of the solution increases, the biosorbent undergoes deprotonation, increasing the negatively charged hydroxyl ions in solution. This increases the biosorbent's Cd removal capacity. In addition, increasing sample dose introduced more sites for the Cd^{2+} ions to bind to, which would lead to an increase in Cd removal.

Treating the peat samples with HCl slightly reduced the ability of four of the six peats to remove Cd from solution, whereas the Cd removal capacities of the remaining two peats increased slightly. One explanation could be that the HCl treatment did not free up enough occupied ion exchange sites for the Cd to bind to. Another explanation could be that the HCl treatment time was not long enough or the HCl solution was not strong enough to free up enough occupied sites (we used 10 % HCl solution for two one-hour treatments).

All six peats were shown to be capable of re-use for Cd biosorption, with or without going through desorption. This means they do not have to be disposed of as hazardous waste after each Cd biosorption cycle, and they may be repeatedly re-used for this purpose. The desorption results demonstrate that some to most of the removed Cd can

be recovered and recycled from all peat types.

The results of this study demonstrate that all six of the peat types tested have high biosorption potential for Cd in aqueous solution. All of the peat types tested demonstrated a great potential for biosorption of Cd from aqueous solutions. The materials are economical, environmentally friendly and readily available. Therefore, peat can be effectively used to remove Cd from contaminated water.

Using highly characterised peats for Cd biosorption resulted in substantial removal of Cd from an aqueous solution. All six of the peat types tested worked well to extremely well at biosorbing Cd from aqueous solutions (36–100 % removal over a variety of factor-manipulated experiments). As sample dose increased from 0.125 g to 0.5 g, the percentage of Cd removed also increased (LS 16 %, OT 26 %, MS 27 %, ON 30 %; RH 24 %; LN 31 %). Increasing contact time from 2 to 48 hours did not significantly affect the Cd biosorption capacities of the peats. As the Cd solution concentration was increased from 1 mg L⁻¹ to 10 mg L⁻¹, the percentage of Cd removed decreased for three of the six peat types tested (MS 23 %, ON 19 %, OT 22 %), while increasing slightly for two of the six peat types tested (LS 1 %, RH 2 %). The last of the peat types tested (LN) did not experience any change in its Cd biosorption capacity when the Cd solution concentration was increased from 1 to 10 mg L⁻¹. As the mixing temperature was increased from 24 °C to 40 °C, the percentage of Cd removed decreased slightly for three of the six peat types tested (OT 4 %, MS 5 %, RH 1 %, LN 13 %), while the other three peat types slightly increased their Cd biosorption capacities (LS 1 %, LN 2 %, ON 12 %). As the pH of the Cd solution was increased from 2 to 10, the percentage of Cd removed increased for all six peat types (MS 57 %, ON 55 %, LS 16 %, OT 55 %, RH 22 %, LN 43 %).

The desorption results showed a 34–71 % Cd recovery rate. Peats re-used for additional Cd biosorption cycles were still highly effective at removing Cd. HCl-treated peats worked slightly worse (four peat types) or slightly better (two peat types) at removing Cd than did the untreated peats.

An exploration of how Cd biosorption varied with key characteristics of the peat samples revealed that the peats with higher calcium and sulphur contents, lower total aldehydes content, and lower values for (humic acids content ÷ fulvic acids content) worked better at removing Cd from aqueous solutions. However, the exact nature of the sorption process is still unclear. The distinction between chemical and physical sorption is a difficult one to make, especially

in cases involving sorption from solutions onto solid sorbents. Dissanayake & Weerasooriya (1981) state that it is the lignin contained within peat that is responsible for creating reactions that trap metal ions. Eskenazy (1970) proposed that the sorption of some metal ions onto peat occurs via chemisorption and suggested that, for the sorption process to be 'chemical', there should be minimal desorption of the sorbed metal ions upon treatment of the peat with 1M HCl. The results obtained from the desorption part of our study show 34–71 % desorption across all of the tested peats, indicating that the sorption process may not be chemical in nature. Other results from our study suggest that the process may be chemical or physical in nature; for example, the fact that as mixing temperature increased, the percentage of Cd removed decreased slightly for three of the six peat types tested, while increasing slightly for the other three peat types.

Comparing selected portions of this study (0.5 g sample dose data only) with the corresponding portions of similar studies with different heavy metals published by this author (Rizzuti *et al.* 2015, 2017) demonstrates that the tested peats work well at removing not only Cd but also hexavalent chromium and mercury. However, these metals were not removed from aqueous solutions equally. All of the peats worked extremely well at removing mercury from solution (95–99 % removal), while only three of the six peats worked as well at removing Cd (96–97 % removal for LN, LS and RH and 66–68 % removal for OT, ON and MS). None of the peats worked as well at removing hexavalent chromium as they did for cadmium and mercury (69–79 % removal across all six tested peats). This may be due to differences in the valence states of the three metals. Nonetheless, the peat samples tested in these three studies demonstrated great potential for biosorption of cadmium, hexavalent chromium and mercury overall.

Organic peat materials have a unique chemical and physical makeup and possess a variety and high number of functional groups, which could possibly explain their affinity for Cd and their consequently high effectiveness in biosorption. Although this is so, using peat for any industrial purpose is increasingly disfavoured nowadays, for sustainability reasons. Nonetheless, studies of the performance of peat in this application are useful because the results can be employed to identify other biological materials - or to develop synthetic adsorbents (i.e. artificial peats) - with properties similar to those of the best-performing peats, for use as biosorbents of Cd. Potential alternative biological materials include agricultural waste products such as soybean hulls or

rice hulls, constructed wetlands with similar plants to those found in the peats utilised in this study (living plants), or possibly biochar of these living plants. Biochar has been found to work fairly well at removing Cd from aqueous solutions (Cui *et al.* 2016) and may possibly work as well as the peats tested in this study. Further research is needed to test these possibilities.

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REFERENCES

- Babel, S. & Kurniawan, T.A. (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials*, B97, 219–243.
- Bailey, S.E., Olin, T.J., Bricka, R.M. & Adrian, D.D. (1999) A review of potentially low-cost sorbents for heavy metals. *Water Research*, 33(11), 2469–2479.
- Brown, P.A., Gill, S.A. & Allen, S.J. (2000) Metal removal from wastewater using peat. *Water Research*, 34(16), 3907–3916.
- Chaney, R.L. & Hundemann, P.T. (1979) Use of peat moss columns to remove cadmium from wastewaters. *Journal (Water Pollution Control Federation)*, 51(1), 17–21.
- Chen, B., Hui, C.W. & McKay, G. (2001) Film-pore diffusion modeling for the sorption of metal ions from aqueous effluents onto peat. *Water Research*, 35(14), 3345–3356.
- Cohen, A.D., Rollins, M.S., Durig, J.R. & Raymond, R. Jr. (1991). Development of a peat sample bank. *Journal of Coal Quality*, 10(4), 145–151.
- Cohen, A.D. & Stack, E.M. (1995) Peat: environmental and energy uses. In: Bisio, A. & Boots, S. (eds.) *Encyclopedia of Energy Technology and the Environment*, John Wiley & Sons Inc., 2205–2218.
- Coupal, B. & Lalancette, J.M. (1976) The treatment of waste waters with peat moss. *Water Research*, 10, 1071–1076.
- Cui, X., Hao, H., Zhang, C., He, Z. & Yang, X. (2016) Capacity and mechanisms of ammonium and cadmium sorption on different wetland-plant derived biochars. *Science of the Total Environment*, 539, 566–575.
- Dissanayake, C.B. & Weerasooriya, S.V.R. (1981) Research Report: Peat as a metal-trapping

- material in the purification of industrial effluents. *International Journal of Environmental Studies*, 17, 233–238.
- Eskenazy, G. (1970) Sorption of beryllium on peat and coals. *Fuel*, 49, 61–67.
- Gupta, V.K., Rastogi, A. & Nayak, A. (2010) Adsorption studies on the removal of cadmium from aqueous solution using a low cost fertilizer industry waste material. *Journal of Colloid and Interface Science*, 342(1), 135–141.
- Krishnani, K., Meng, X., Christodoulatos, C. & Boddu, V. (2008) Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. *Journal of Hazardous Materials*, 153, 1222–1234.
- Li, C. & Champagne, P. (2009) Fixed-bed column study for the removal of cadmium (II) and nickel (II) ions from aqueous solutions using peat and mollusk shells. *Journal of Hazardous Materials*, 171, 872–878.
- McLellan, J.K. & Rock, C.A. (1986) The application of peat in environmental pollution control: a review. *International Peat Journal*, 1, 1–14.
- Meena, A.K., Kairvelu, K., Mishra, G.K., Rajagopal, C. & Nagar, P.N. (2008) Adsorptive removal of heavy metals from aqueous solution by treated sawdust (*Acacia arabica*). *Journal of Hazardous Materials*, 150, 604–611.
- Rizzuti, A.M., Cohen, A.D. & Stack, E.M. (1996) Effects of irradiating peats on their ability to extract BTEX and cadmium from contaminated water. *Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering*, A31(8), 1917–1949.
- Rizzuti, A.M., Eltayeb, S., Cohen, A.D., Stack, E.M., Liu, J. & Durig, J.R. (2003) Using highly characterized peats to extract heavy metal ions from contaminated water. *International Peat Journal*, 11, 3–13.
- Rizzuti, A.M. Ellis, F.L., Cosme, L.W., & Cohen, A.D. (2015) Biosorption of mercury from aqueous solutions using highly characterised peats. *Mires and Peat*, 16(02), 1–7.
- Rizzuti, A.M. Newkirk, C.R., Wilson, K.A., Cosme, L.W. & Cohen, A.D. (2017) Biosorption of hexavalent chromium from aqueous solutions using highly characterised peats. *Mires and Peat*, 19(04), 1–10.
- Stack, E.M., Eltayeb, S., Liu, J., Cohen, A.D. & Durig, J.R. (1996) The use of characterized peats as sorption media for heavy metals. In: Tedder, D.W. & Pohland, F.G. (eds.) *Emerging Technologies in Hazardous Waste Management VI*, American Chemical Society, Washington DC, 1001–1005.
- Teker, M., Imamoglu, M. & Saltabas, O. (1999) Adsorption of copper and cadmium ions by activated carbon from rice hulls. *Turkish Journal of Chemistry*, 23, 185–191.
- Volesky, B. (2007) Biosorption and me. *Water Research*, 41(18), 4017–4029.

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Appendix: Key characteristics of the peat types used in this research, from Rizzuti *et al.* (2017). ASTM: American Society for Testing and Materials (international standards organisation); FL: Florida; GA: Georgia.

| Sample code | Peat type | | | | | |
|------------------------------------|--------------------------|---|---|------------------------------------|------------------------------------|--|
| | MS | ON | LS | OT | RH | LN |
| Sample name | Maine <i>Sphagnum</i> | Okefenokee <i>Nymphaea</i> | Loxahatchee Sawgrass | Okefenokee <i>Taxodium</i> | Shark River <i>Rhizophora</i> | Loxahatchee <i>Nymphaea</i> |
| Location of origin | Maine | Okefenokee Swamp, GA | Loxahatchee WL Refuge, FL | Okefenokee Swamp, GA | Everglades National Park, FL | Loxahatchee WL Refuge, FL |
| Dominant botanical components | <i>Sphagnum</i> | <i>Nymphaea</i> , <i>Sagittaria</i> , grass-sedge | Grass-sedge, <i>Nymphaea</i> , fern | <i>Taxodium</i> , <i>Persea</i> | <i>Rhizophora</i> | <i>Nymphaea</i> , <i>Sagittaria</i> |
| ASTM classification fibre (area-%) | Fibric (81) | Hemic (50) | Hemic (48) | Sapric (18) | Hemic (55) | Hemic (40) |
| Ca (wt-%) | 0.03 | 0.02 | 2.17 | 0.02 | 1.17 | 1.80 |
| Ash (wt-%) | 0.8 | 12.4 | 7.2 | 12.8 | 31.0 | 6.4 |
| S (wt-%) | 0.11 | 0.37 | 0.96 | 0.29 | 2.72 | 0.69 |
| Total aldehydes (%) | 12.891 | 13.837 | 8.112 | 11.021 | 7.061 | 8.012 |
| Total furans (%) | 2.926 | 4.730 | 5.046 | 6.259 | 2.851 | 5.255 |
| Total furanones (%) | 15.068 | 4.592 | 4.363 | 3.376 | 5.720 | 7.791 |
| Total pyranones (%) | 7.478 | 9.143 | 1.551 | 3.416 | 5.701 | 5.250 |
| Total other ketones (%) | 3.548 | 2.753 | 2.949 | 3.329 | 1.578 | 4.842 |
| Total guaiacyl lignins (%) | 10.529 | 12.537 | 12.580 | 13.865 | 14.225 | 13.172 |
| Total other lignins (%) | 18.683 | 9.244 | 16.767 | 13.432 | 13.067 | 10.477 |
| Humic acids content (%) | 5.5 | 4.9 | 4.6 | 14.5 | 2.7 | 7.1 |
| Fulvic acids content (%) | 0.06 | 0.02 | 0.12 | 0.27 | 0.74 | 0.20 |
| Humic/fulvic acids ratio | 92 | 245 | 38 | 54 | 4 | 36 |