Biosorption of hexavalent chromium from aqueous solutions using highly characterised peats

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SUMMARY

This research investigated the biosorption of hexavalent chromium (Cr^{VI}) from aqueous solutions by six highly characterised peats. Samples of the peats were tested both in unaltered condition and after being treated with hydrochloric acid (HCl) to free up any occupied exchange sites. Other variables tested were sample dose, contact time, mixing temperature, and the concentrations and pH of the Cr^{VI} solution. Desorption studies were also performed, and tests were done to determine whether the peats could be re-used for Cr^{VI} biosorption. The results indicate that all six peat types biosorb Cr^{VI} from aqueous solution well (42–100 % removal) and that their Cr^{VI} removal capacities are affected by manipulation of the various factors. The two factors that had the greatest impact on the Cr^{VI} removal capacities of the peats were the concentrations and pH of the Cr^{VI} solution. As the Cr^{VI} solution concentration and pH were increased, the percent of Cr^{VI} removed decreased dramatically (33–56 % decrease for concentration increase; 36–45 % decrease for pH increase with four of the six peat types). The desorption results indicate that it may be possible to recover up to 5 % of the removed Cr^{VI}. All of the peat types tested can be repeatedly re-used for additional Cr^{VI} biosorption cycles. Hence, their disposal should not become a hazardous waste problem.

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

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INTRODUCTION

Industrial wastewater effluents containing heavy metals are a major source of water pollution. Industries such as metal plating, mining, oil refining, rubber processing, tanning and chemical manufacturing all contribute to this problem (Meena *et al*. 2008). Metals such as lead, cadmium, chromium (VI) and mercury have the highest toxicities. Traditional heavy metal waste removal techniques such as ion exchange and precipitation, reverse osmosis, electrodialysis, lime coagulation, and adsorption using activated carbon and lime ash are not efficient because they are costly and have high energy input requirements. Metals may not be completely removed when these methods are applied, and toxic sludge can be generated (Krishnani *et al*. 2008). There is a need for cost-effective, environmentally friendly heavy metal remediation technologies.

Biosorption is a fairly new technique that has been presented as both effective and inexpensive in comparison to chemical and physical technology (Krishnani *et al*. 2008). In addition, various biosorbent materials have been found to work well at removing heavy metals from aqueous solutions. Biosorption is the binding of metal ions and radionuclides onto the cellular structures of biological materials, including their ligands and functional groups. Biosorbent materials that are lignocellulosic (containing cellulose, hemicellulose and lignin) have high adsorption properties due to their ion exchange capabilities. Accordingly, they can be used as productive biosorbent material (Krishnani *et al*. 2008). It has 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. The efficacy of biosorbent materials 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 sediment derived from plants. Several studies have shown that peats are effective at removing heavy metals from aqueous solutions. Four papers present good reviews of the literature up to 2003 (McLellan & Rock 1986, Bailey *et al*. 1999, Brown *et al*. 2000, Babel & Kurniawan 2003), and additional relevant references include Chen *et al*. (2001). Several studies including our own (Stack *et al*. 1994, Cohen & Stack 1995, Rizzuti *et al*.

1996, Rizzuti *et al*. 2003, Rizzuti *et al*. 2015) have shown that the amounts and rates of metal extraction can differ greatly between one type of peat and another. This is due to the fact that 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 Cr^{VI} removal capacity of peat (Sharma & Foster 1993, Coupal & Lalancette 1976, Tummavuori & Aho 1980). In these studies the Cr^{VI} removal capacities of only moss (e.g. *Sphagnum*) peats were tested.

The United States of America (USA) Environmental Protection Agency (EPA) has set the maximum contaminant level goal for Cr^{VI} in drinking water at 100 ppb. The study reported here was funded by the Department of Energy (DOE) to develop cost-effective, environmentally friendly Cr^{VI} remediation techniques, specifically in the context of waterborne Cr^{VI} being discharged into water sources from the Hanford DOE site in Richland, Washington (USA). The purpose of this study was to determine the capacities of six different highly characterised peat types for biosorption of Cr^{VI} from aqueous solutions at concentrations typical of those observed at Hanford (within the range 1–30 ppm).

MATERIALS AND METHODS

Materials
The peats were obtained from the peat sample bank at Claflin University. Six different peat types were used. They were chosen to represent a wide range of depositional environments and chemical and physical properties (Table 1).

The Cr^{VI} solutions were prepared by diluting a 100 ppm stock solution (in 5 % nitric acid) to the desired concentrations in parts per million (ppm) using ASTM Type II deionised water. The concentration of the initial working standard was 10 ppm.

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, 0.25 g of peat was weighed out, placed in a 125 ml flask, and 50 ml of 10 ppm Cr^{VI} solution was added. The flask was then placed on a shaker (Thermo Scientific MaxQ 2000) at ~ 175 rpm to mix for 24 hours. In order to test the effects of different factors on the removal of Cr^{VI},

we varied the quantity of peat, the concentration of the Cr^{VI} solution, the mixing time, and other factors. Details of the various treatments that were applied are given below.

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 10 ppm (pH 1.4) Cr^{VI} solution for 24 hours.

Contact time
To study the effect of contact time, 0.25 g of each peat type was mixed with 50 ml of 10 ppm (pH 1.4) Cr^{VI} solution for 2, 24 or 48 hours.

Mixing temperature
To determine the effect of mixing temperature, 0.25 g of peat was mixed with 50 ml of 10 ppm (pH 1.4) Cr^{VI} solution for 24 hours in a temperature-controlled shaker set at room temperature (24 ± 1 °C), 30 °C, 35 °C or 40 °C.

Cr^{VI} solution concentration
To investigate the effect of Cr^{VI} solution concentration, 0.25 g of each peat type was mixed with 50 ml of 1, 5, 10, 20 or 30 ppm (pH 1.4) Cr^{VI} solution for 24 hours. These (low) concentrations were chosen to represent the waterborne Cr^{VI} concentrations found in water sources surrounding the Hanford DOE site.

pH of Cr^{VI} solution
To test the effect of varying pH of the Cr^{VI} solution, 0.25 g of each peat type was mixed with 50 ml of 10 ppm hexavalent chromium solution at different pHs in the range 2−10 (increment unity) for 24 hours. This was achieved by adjusting the pH of the working Cr^{VI} solution above or below that of the initial working standard solution (1.4 ± 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 sites to bond with Cr^{VI} 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, 0.25 g of the HCl-treated peat sample was mixed with 50 ml of a 10 ppm (pH 1.4) Cr^{VI} solution for 24 hours.

Desorption of Cr^{VI}
To determine whether the removed hexavalent chromium could be recovered and recycled, peat samples that had been used for the biosorption of hexavalent chromium were tested to determine the

Table 1. Key characteristics of the peat samples used in this research (Cohen *et al.* 1991). 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 *Sphagnum*	Okefenokee *Nymphaea*	Loxahatchee Sawgrass	Okefenokee *Taxodium*	Shark River *Rhizophora*	Loxahatchee *Nymphaea*
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	*Sphagnum*	*Nymphaea, Sagittaria,* grass-sedge	Grass-sedge, *Nymphaea,* fern	*Taxodium, Persea*	*Rhizophora*	*Nymphaea, Sagittaria*
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

amount of hexavalent chromium that could be desorbed from them afterwards. Peat that had already been used once for biosorption of Cr^{VI} (0.25g of sample mixed for 24 hours with 10 ppm hexavalent chromium solution at pH 1.4) were mixed with 100 ml of a 10 % HCl solution for two hours.

Re-using samples for biosorption of Cr^{VI}

Peat samples that had been used for biosorption of Cr^{VI} were also tested to determine whether they could be re-used for this purpose and whether desorbing the Cr^{VI} from the peat would improve its effectiveness when re-used. Samples were tested (with and without going through desorption) for their Cr^{VI} removal capacities after being used once. Peat that had already been used once for biosorption of Cr^{VI} (24 hours with 10 ppm Cr^{VI} solution at pH 1.4) was mixed with 50 ml of fresh 10 ppm Cr^{VI} solution (pH 1.4) for 24 hours.

Measurement of hexavalent chromium remediation

After shaking, the Cr^{VI} 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 their Cr^{VI} concentrations. The Cr^{VI} concentration was measured using Inductively Coupled Plasma (Teledyne Leeman Labs, NH). Before each analysis session, calibration standards (1, 5, 10, 20 and 30 ppm) were freshly prepared from the 100 ppm Cr^{VI} stock solution and used to establish a standard calibration curve.

RESULTS

The results (Table 2) demonstrate that all six peat types worked well at biosorbing Cr^{VI} from aqueous solutions (42–100 % removal). The concentration and pH of the Cr^{VI} solution had the greatest effect on the Cr^{VI} removal capacities of the peats. Overall, manipulation of the various factors tested had at least some effect on the Cr^{VI} removal capacities of the peats.

Effect of sample dose

Mixing with a small amount (0.125 g) of all peat types resulted in a substantial removal of Cr^{VI} from the aqueous solutions (58–70 %). As the sample dose was increased from 0.125 g to 0.5 g the percentage of Cr^{VI} removed increased slightly (5–10 % increase). The greatest increase (10 %) was for MS peat.

Effect of contact time

For all of the peat samples, increasing contact time from 2 hours to 48 hours decreased their Cr^{VI} removal capacities (73 to 59 % for MS; 78 to 64 % for ON; 77 to 66 % for OT; 80 to 70 % for LS; 76 to 65 % for RH; 83 to 69 % for LN). All of the six peats reached their maximum Cr^{VI} removal capacity after a contact time of 2 hours.

The kinetic curves (Figure 1) show that the removal of Cr^{VI} by all peat types occurred in a two-stage process. The first stage is characterised by a rapid uptake that occurs during the first two hours of contact, and it is followed by a second stage of slight release of biosorbed Cr^{VI} during the next 46 hours.

Effect of mixing temperature

As the mixing temperature was increased from 24 °C to 40 °C, the percentage of Cr^{VI} removed decreased slightly for all peats (4–13 % decrease). The greatest decrease (13 %) was for LN peat.

Effect of hexavalent chromium solution concentration

Increasing the Cr^{VI} solution concentration from 1 ppm to 30 ppm significantly decreased the Cr^{VI} removal capacities of the peats. (99 to 43 % for MS; 100 to 56 % for LS; 96 to 51 % for OT; 93 to 50 % for ON; 98 to 57 % for RH; 92 to 59 % for LN). The greatest decrease (56 %) was for MS peat.

Effect of pH of hexavalent chromium solutions

As the pH of the Cr^{VI} solution was increased from 2 to 10, the Cr^{VI} removal capacities of the peat samples decreased significantly for five of the six peats, while increasing for one peat type. As the pH of the Cr^{VI} solution increased from 2 to 10, the largest change in percentage of Cr^{VI} removed occurred with RH peat (90 % at pH 2 to 45 % at pH 10). Cr^{VI} removal decreased from 95 % at pH 2 to 51 % at pH 10 with LS peat; from 92 % at pH 2 to 49 % at pH 10 with LN peat; from 90 % at pH 2 to 54 % at pH 10 with OT peat; and from 89 % at pH 2 to 70 % at pH 10 with ON peat. The Cr^{VI} removal capacity of MS peat increased as the pH of the Cr^{VI} solution increased from 2 to 10, from 86 % at pH 2 to 95 % at pH 10.

Effect of HCl treatment

Treating the peat samples with HCl slightly increased their ability to remove Cr^{VI} from solution (4–7 % increase). The OT peat experienced the largest increase in its Cr^{VI} removal capacity after being treated with HCl (69 % for unaltered sample and 76 % for HCl treated sample).

Table 2. Percent hexavalent chromium 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	58	64	69	65	70	70
	0.250	63	68	74	69	72	74
	0.50	69	72	77	73	75	79
Contact time (hr)	2	73	78	80	77	76	83
	24	63	68	74	69	72	74
	48	59	64	70	66	65	69
Mixing temperature (°C)	24	63	68	74	69	72	74
	30	59	65	69	67	69	73
	35	59	66	67	64	64	64
	40	56	64	65	64	65	61
Concentration (ppm) of hexavalent chromium solution	1	99	93	100	96	98	92
	5	74	77	82	80	79	81
	10	63	68	74	69	72	74
	20	50	56	61	57	64	64
	30	43	50	56	51	57	59
pH	2	86	89	95	90	90	92
	3	98	96	74	86	83	58
	4	99	97	67	71	59	45
	5	99	96	53	78	45	52
	6	96	75	65	67	43	47
	7	96	92	67	67	49	43
	8	96	90	50	59	46	42
	9	96	82	42	72	49	44
	10	95	70	51	54	45	46
HCl treatment	without	63	68	74	69	72	74
	with	67	74	80	76	76	80
Re-use	first use	63	68	74	69	72	74
	after desorption	65	69	73	71	73	74
	without desorption	56	61	65	64	66	60
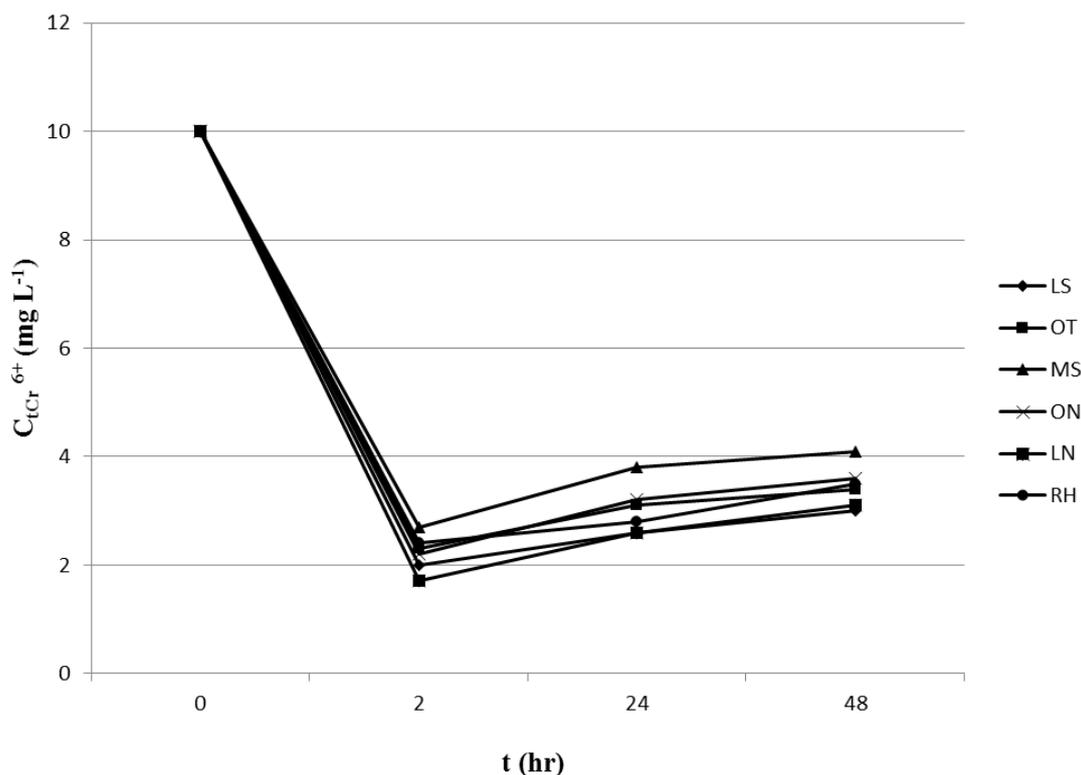
Figure 1. Values of the concentration of Cr^{VI} in solution (C_{tCr}^{6+}, mg L^{-1}) plotted against time (t, h) for a C_{0Cr}^{6+} of 10 mg L^{-1}.

Desorption of hexavalent chromium

The desorption results indicate that it may be possible to recover and recycle some of the removed Cr^{VI} from the peat samples. The MS peat had 5 % of the Cr^{VI} desorbed; ON, LS, RH and LN had 4 %; and OT had 3 % desorption.

Re-use of samples for biosorption

There was a slight increase in Cr^{VI} bisorption between samples that were re-used after going through desorption and samples being re-used without going through desorption (7–13 % increase). The greatest increase (13 %) was for LN peat (60 % when re-used without desorption and 73 % Cr^{VI} removal when re-used after desorption). MS peat had 56 % Cr^{VI} removal when re-used without desorption and 65 % Cr^{VI} removal when re-used after desorption. LS peat had 65 % Cr^{VI} removal when re-used without desorption and 73 % Cr^{VI} removal when re-used after desorption. ON peat had 61 % Cr^{VI} removal when re-used without desorption and 69 % Cr^{VI} removal when re-used after desorption. OT peat had 64 % Cr^{VI} removal when re-used without desorption and 71 % Cr^{VI} removal when re-used after desorption. LS peat had 65 % Cr^{VI} removal when re-used without desorption

and 73 % Cr^{VI} removal when re-used after desorption. RH peat had 66 % Cr^{VI} removal when re-used without desorption and 73 % Cr^{VI} removal when re-used after desorption. These results indicate that all six peat types can be re-used for Cr^{VI} biosorption, whether or not they undergo desorption in between the two biosorption cycles.

In order to determine which physical or chemical characteristics of the six tested peat types might be related to their Cr^{VI} removal capacity, key characteristics of the peat samples (listed in Table 1) were plotted against their Cr^{VI} removal results (0.25 g of each peat type mixed with 50 ml of 10 ppm (pH 1.4) Cr^{VI} solution for 24 hours). Only four of the key characteristics correlated well with the Cr^{VI} removal results. These four characteristics were calcium content, sulphur content, total aldehydes content, and the ratio of humic acids content to fulvic acids content. In general, as the calcium and sulphur contents of the peat types increased, their Cr^{VI} removal capacities increased as well (Figure 2 and Figure 3). In contrast, as the total aldehydes content and the ratio of humic acids to fulvic acids content of the peat types increased, their Cr^{VI} removal capacities decreased (Figure 4 and Figure 5).
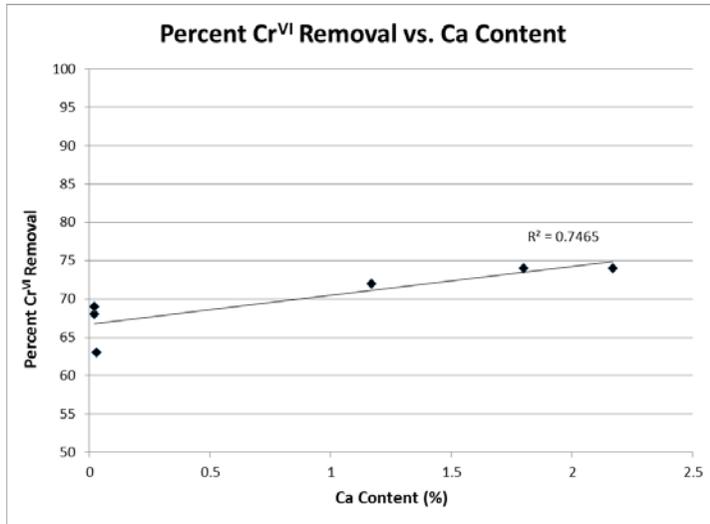
Figure 2. Percent Cr^{VI} removal *versus* calcium content.
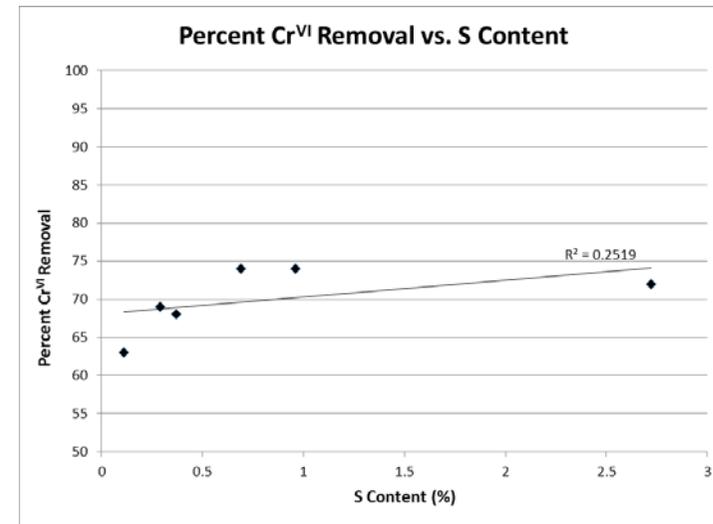

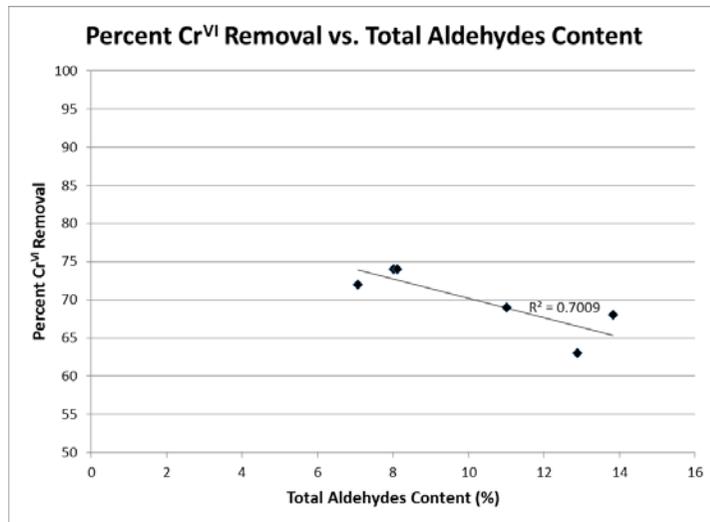Figure 3. Percent Cr^{VI} removal *versus* sulphur content.

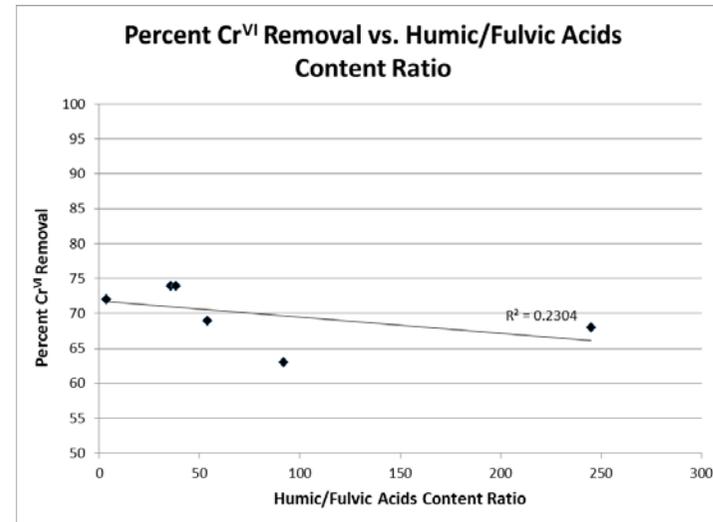Figure 4. Percent Cr^{VI} removal *versus* total aldehydes content.

Figure 5. Percent Cr^{VI} removal *versus* humic/fulvic acids content ratio.

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 Cr^{VI} from aqueous solutions is the high affinity of their functional groups (Table 1) for Cr^{VI}. These polar functional groups appear to be capable of removing large amounts of Cr^{VI} ions from aqueous solutions.

Manipulating various factors affected the Cr^{VI} removal capacities of the peats. Of the factors whose effects were tested here, the concentration and pH of the Cr^{VI} solution had the greatest impact on Cr^{VI} removal capacities. Both the surface charge of the adsorbent material and the level of ionisation and speciation of the metal are affected by pH (Teker *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 Cr^{VI} removal is 2 for four of the six peat types (LS, OT, LN, and RH).

The ON peat worked best at removing Cr^{VI} when the pH of the Cr^{VI} solution was 4, while the MS peat worked best when the pH of the Cr^{VI} solution was in the range 4–5. An explanation could be that, at lower pH, the biosorbent is positively charged due to protonation and Cr^{VI} exists in the form of oxyanions such $HCr_2O_7^-$, $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-} in acidic media leading to an electrostatic attraction between them (Gupta *et al.* 2010). As the pH of the solution increases, the biosorbent undergoes deprotonation, increasing the negatively charged hydroxyl ions in solution. This reduces the Cr^{VI} removal capacity of the biosorbent. Using three of the peat types (LS, LN and RH), Cr^{VI} removal decreased when the pH of the Cr^{VI} solution was ≥ 8. According to Meena *et al.* (2008), this may be due to formation of soluble hydroxyl complexes.

Treating the peats with HCl had little effect on their ability to remove Cr^{VI} from solution. One explanation could be that the HCl treatment did not free up enough occupied sites for the Cr^{VI} 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 applied two one-hour treatments with a 10 % solution of HCl).

All peats were shown to be capable of re-use for Cr^{VI} biosorption, with or without going through desorption (although they were slightly more effective after going through desorption). This means they do not have to be disposed of as a hazardous waste after each Cr^{VI} biosorption cycle, and they may be repeatedly re-used for this purpose. The desorption results demonstrate that some of the removed Cr^{VI} 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 Cr^{VI} in aqueous solution. The materials are economical, environmentally friendly and readily available. Therefore, peat can be effectively used to remove Cr^{VI} from contaminated water. Using highly characterised peats for Cr^{VI} biosorption resulted in substantial removal of Cr^{VI} from an aqueous solution. All six peat types tested worked extremely well at biosorbing Cr^{VI} from aqueous solutions (42–100 % removal, over a variety of factor-manipulated experiments). As the sample dose was increased from 0.125 g to 0.5 g the percent of Cr^{VI} removed increased slightly (LS 8 %; OT 8 %; MS 10 %; ON 8 %; RH 6 %; LN 9 %). As contact time increased from 2 hours to 48 hours, the percent of Cr^{VI} removed decreased (LS 10 %; OT 11 %; MS 14 %; ON 14 %; RH 9 %; LN 14 %). As the concentration of the Cr^{VI} solution was increased from 1 ppm to 30 ppm, the percent of Cr^{VI} removed decreased dramatically (LS 44 %; OT 45 %; MS 56 %; ON 43 %; RH 41 %; LN 33 %). As the mixing temperature was increased from 24 °C to 40 °C, the percent of Cr^{VI} removed decreased slightly (LS 9 %; OT 5 %; MS 6 %; ON 4 %; RH 7 %; LN 13 %). The mixing temperature results demonstrate that the Cr^{VI} removal was exothermic in nature. As the pH of the Cr^{VI} solution was increased from 2 to 10 the percent of Cr^{VI} removed fluctuated, but generally decreased, for four of the six peat types (LS 44 %; OT 36 %; RH 45 %; LN 43 %), while increasing slightly for one of the peat types (MS 9 %), and fluctuating sporadically but generally decreasing, for the last peat type (ON 19 %). The desorption results showed only a 3–5 % Cr^{VI} recovery rate. Peats re-used for additional Cr^{VI} biosorption cycles were still highly effective at removing Cr^{VI} (with or without going through desorption, although slightly more effective after going through desorption). HCl-treated peats worked slightly (4–7 %) better at removing Cr^{VI} than did the untreated peats. Correlations with key characteristics of the peat samples revealed that the peats with higher calcium and sulphur contents, lower total aldehydes content, and lower humic acids to fulvic acids content ratios worked better at removing Cr^{VI} 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 to solid sorbents. Dissanayake & Weerasooriya (1981) state that it is the lignin contained within peat that is responsible for creating reactions which trap metal ions. Eskenazy (1970) proposed that the sorption of some metal ions onto peat occurs *via* chemisorption. For the sorption process to be 'chemical', Eskenazy suggested that 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 only 3–5 % desorption for all tested peats, which indicates that the sorption process may be chemical in nature. On the other hand, other results from our study indicate that the process may be physical in nature. These include the fact that the maximum Cr^{VI} removal was achieved within a two-hour period by all tested peats. Overall, all of the peat types tested demonstrated a great potential for biosorption of Cr^{VI} from aqueous solutions. Organic peat materials have a unique chemical and physical makeup (Table 2) and possess a variety and high number of functional groups, which could possibly explain their greater affinity for Cr^{VI} biosorption.

ACKNOWLEDGEMENTS

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