SPHAGNUM MOSS PEAT

AS A POTENTIAL SORBENT AND REDUCTANT

FOR CHROMIUM (VI) REMOVAL FROM AQUEOUS SOLUTIONS

CATALIN BALAN, DOINA BILBA and MATEI MACOVEANU

"Gh. Asachi" Technical University, Faculty of Chemical Engineering and Environmental
Protection, Department of Environmental Engineering and Management,
71A,D. Mangeron Blvd., 700050 Iaşi, Romania

Batch sorption experiments were carried out for the removal of chromium (VI) ions from aqueous solutions using the Romanian *sphagnum* moss peat. Similar to many biomaterials, peat removes Cr (VI) by a mechanism of "sorption-coupled reduction", involving both the sorption, in acidic media, of the hydrochromate anion on the peat surface and the reduction, in the solution, of toxic Cr (VI) to less toxic Cr (III). Reduction and sorption processes were investigated as a function of the initial pH of the solution, peat dose, metal ion concentration and contact time. Removal of Cr (VI) is enhanced by lower pH values (pH = 1-2), while a peat dose of 8 g/L assures an almost complete removal of Cr (VI) from solutions with an initial concentration of 50 mg/L. The experimental results point out the potential of *sphagnum* moss peat, an available natural material, in removing Cr (VI) from wastewater.

Keywords: *sphagnum* moss peat, Cr (VI), sorption, reduction

INTRODUCTION

The extensive use of chromium in several industrial activities – including electroplating, leather tanning, electric-power production, pulp production, paint and pigment manufacturing, and ore and petroleum refining – has produced significant quantities of chromium wastes, which can generate a considerable pollution of both water and soil.

In the environment, chromium exists in two main stable oxidation states, Cr (III) and Cr (VI), which form different ionic species.[1] Depending on the pH values of the aqueous solution, Cr (VI) may be present as hydrochromate ($HCrO_4^-$), cromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$), and Cr (III) – as hydrated trivalent chromium ($Cr(H_2O)_6^{3+}$) and chromium hydroxide complexes ($Cr(OH)(H_2O)_5^{2+}$ and $Cr(OH)_2(H_2O)_4^+$). The toxicity of the soluble chromium species and their mobility in aquatic and terrestrial envi-

ronments depend on their oxidation state. Cr (VI), very mobile in the environment and highly toxic, is carcinogenic and mutagenic to living organisms, while Cr (III) is considered an essential trace element, less toxic and less mobile than Cr (VI) (at neutral pH Cr (III) forming insoluble chromium hydroxide).[2,3] The tolerance limit for aqueous effluents discharge into inland waters[4] is of 1.0 mg/L for total chromium (Cr (III) and Cr (VI)), and of 0.1 mg/L for Cr (VI).

Several treatment technologies, such as chemical precipitation,[5] ion exchange,[6] solvent extraction,[7] membrane separation[8] and adsorption,[9] have been developed for the removal of hexavalent chromium from water and wastewaters, prior to disposal. Chemical precipitation, the most frequently applied method, involves the reduction of Cr (VI) to Cr (III) and the subsequent precipitation of

Cr (III) as hydroxide, sulphide or carbonate; the process uses many chemicals, is complicated and time consuming, has a poor efficiency and generates large amounts of chemical sludge. Ion exchange and activated carbon adsorption represent available and effective treatment methods for solutions with medium and low concentrations (1-100 mg/L), but they are expensive, requiring higher capital investments. The high cost of the commercial activated carbons has stimulated the search of cheaper alternatives and, recently, a variety of non-conventional and low-cost materials, such as agricultural or industrial wastes/by-products,[9-12] clay minerals,[13] biomasses[14,15] and peat,[16,17] have been employed as sorbents for hexa- and trivalent chromium remediation from water. Most studies explained the removal of Cr (VI) by biomaterials through an anionic adsorption mechanism (the anionic Cr (VI) species bind to the positively charged groups of the sorbent).[9] Recently, Park *et al*.[18,19] suggested that the mechanism of Cr (VI) biosorption by natural biomaterials is an "adsorption-coupled reduction".

Peat is a heterogeneous mixture of more or less decomposed plant materials accumulated in poorly oxygenated wetlands. The composition of peat from different peatlands varies considerably with the environmental conditions during its formation (nature of original vegetation, climate, water acidity) as well as with the degree of decomposition. The major constituents of peat, namely lignin, cellulose and humic substances, contain structural moieties groups, such as –OH, –COOH, =C=O, –C–O–C–, capable of taking part in protolytic, ion exchange and complexation reactions with sorbed pollutant species.[17] The ability of peat to remove heavy metals such as copper, cadmium, lead, nickel, chromium, has been reported by several authors.[16,17,20-26]

In the present study, the capacity of Romanian *sphagnum* moss peat to remove chromium (VI) ions was investigated under batch conditions, involving process parameters such as initial pH, peat dose, chromium concentration and contact time. The analysis of both Cr (VI) and total Cr in the aqueous phase was used to establish the contributions of adsorption and redox processes in chromium removal.

EXPERIMENTAL
Materials
A commercially available *sphagnum* moss peat (Poiana Stampei, Romania) was used. The material was air-dried, grounded and sieved to 1-2 mm particle size. The main peat characteristics were determined according to standard methods, the results obtained (Table 1) suggesting a peat with a low degree of decomposition.

The stock solution of Cr (VI) (1040 mg/L) was prepared using analytical reagent grade potassium dichromate ($K_2Cr_2O_7$) (Sigma), in distilled water. All working solutions were prepared by adequate dilution of the stock solution with distilled water.

Sorption experiments
Batch sorption experiments were performed in 250 mL conical flasks by shaking the required amount of peat with 50 mL aqueous solutions of Cr (VI) of a known concentration, at a constant temperature (20 ± 1 °C). The initial pH of the solutions, adjusted to a constant value by the addition of H_2SO_4 diluted solutions, was measured with a pH-meter RADELKIS OP-271 pH/Ion analyzer. After a specified contact time period, the peat was separated by filtration and the residual concentration of Cr (VI) in solution was spectrophotometrically analyzed using 1,5-diphenylcarbazide in acidic solution at $\lambda = 540$ nm (UV-VIS Digital Spectrophotometer, model S 104D /WPA). To determine the total Cr concentration, Cr (III) was first oxidized to Cr (VI), at a high temperature, with potassium permanganate. Cr (III) concentration was calculated as the difference between the total Cr and Cr (VI) concentrations.

The efficiency of Cr (VI) removal was assessed by the residual concentrations in chromium, C (mg/L) (total, Cr (VI) and Cr (III)) and by the removal percent, R (%) (total, sorption and reduction).

The influence of the operating process parameters was investigated according to the conditions listed in Table 2.

Table 1
Characteristics of *sphagnum* moss peat

Properties	Value
pH (1:50, w:v deionized water)	4.05 ± 0.05
pH$_{ZPC}$	3.7
Ash content (wt %)	4.85
Organic matter (wt %)	84-85
Moisture content (wt %)	10.5-11
Cation exchange capacity (meq/g of peat)[*]	0.575

[*]determined by pH-metric titration in a 0.1 M NaCl solution

Table 2
Experimental conditions applied in Cr (VI) removal by *sphagnum* moss peat

| Operating variable	Initial pH	Amount of peat (g/L)	Concentration of Cr (VI) (mg/L)	Contact time (h)
Effect of pH	1-5.5	4	20.8	24
Effect of peat dose	2	4-20	52	24
Effect of Cr (VI) concentration	2	4	20-100	24
Effect of contact time	2	4	52	15 min - 4 h

RESULTS AND DISCUSSION

Effect of solution pH

It is expected that the initial solution pH is an important controlling parameter in the removal of Cr (VI), influencing not only sorption (by the speciation of heavy metals in the solution and by the surface charge of the sorbent), but also the reduction of Cr (VI) to Cr (III). According to the speciation diagram[9] of Cr (VI), in aqueous solutions with pH = 1-6 and concentrations below 1 g/L, hexavalent chromium is present as the hydrochromate anion $HCrO_4^-$. The effect of the initial pH on Cr (VI) removal was studied on solutions of 20.8 mg Cr/L concentration, with pH varying from 1 to 5.5. The relation between the initial pH of the solutions and the residual concentrations of chromium is plotted in Figure 1.

After 24 h of phase contact, in a solution of pH = 1, the concentration of Cr (VI) is close to zero, the solution containing 11.3 mg Cr (III)/L; the difference up to 20.8 mg/L corresponds to the Cr (VI) retained by sorption on the peat surface. As the initial pH of the solution increases up to 4, the concentration of Cr (VI) in the solution increases too, while the concentration of Cr (III) decreases. In solutions with pH = 4-5.5, the initial and residual concentrations of Cr

(VI) are identical, and Cr (III) is not present. This behaviour shows[27] that both processes – sorption and reduction – take place simultaneously, being strongly dependent on the solution pH.

Figure 2 presents the influence of the initial pH value on Cr (VI) sorption and reduction by peat. The efficiency of Cr (VI) removal is the highest in solutions of pH = 1-2, when about half of the initial amount of Cr (VI) is adsorbed on peat, the other half remaining in solution as Cr (III), which is less toxic. Cr (VI) sorption sharply decreases with the increase in pH from 3 to 5.5. This behaviour may be correlated with the ionic state of the functional groups present on the peat surface. The obtained value of the pH$_{ZPC}$ (zero point charge) of the used peat was of 3.7. Below this pH value, the active sites of peat are positively charged (oxygen is easily protonated under acidic conditions) and susceptible to electrostatic interactions with the $HCrO_4^-$ anions:

$$Peat\text{-}OH + HCrO_4^- + H^+ \rightleftarrows Peat\text{-}OH_2^+HCrO_4^- \quad (1)$$
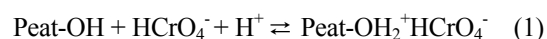
At a pH higher than the pH$_{ZPC}$ value, the peat surface is negatively charged, due to the dissociation of the carboxylic groups, being unavailable to bind $HCrO_4^-$ anions.
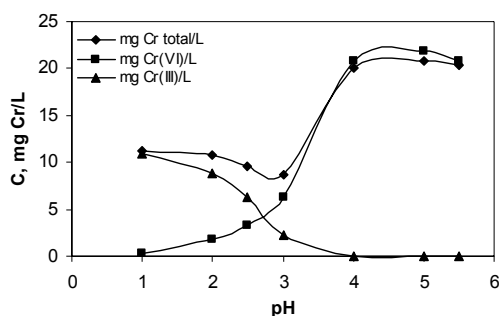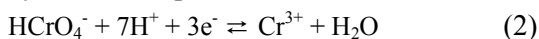
Figure 1: Effect of initial solution pH on the residual concentrations of Cr species: $C_0 = 20.8$ mg/L, peat dose = 4 g/L, time = 24 h

Figure 2: Effect of solution pH on the removal, reduction and sorption of Cr (VI): $C_0 = 20.8$ mg/L, peat dose = 4 g/L, time = 24 h

Figure 2 also shows that, as the solution pH increases (from 1 to 4), the reduction of Cr (VI) decreases from 52 to 0%. It is known[28] that, once in contact with biomaterials, especially in acidic solutions, Cr (VI) can be easily or spontaneously reduced to Cr (III). The high value of the positive redox potential of Cr (VI) (pH = 1, $E^0 = 1.33$ V) indicates a strong oxidant, unstable in the presence of electron donors; the most probable reaction partners of Cr (VI) are the humic substances from peat.[29]

The reduction of Cr (VI) is accompanied by H^+ consumption:

$$HCrO_4^- + 7H^+ + 3e^- \rightleftarrows Cr^{3+} + H_2O \qquad (2)$$

and thus the initial solution pH decreases the formal potential and the oxidizing capacity of Cr (VI), concomitantly with decreasing Cr (III) concentration and the reduction
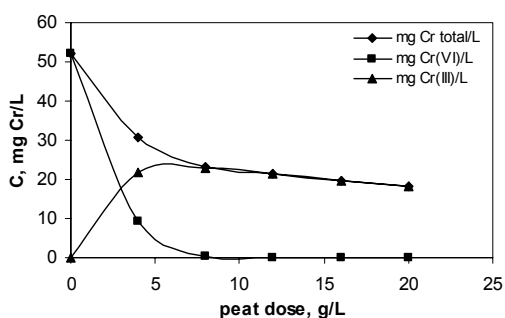
percentage. A significant decrease of Cr (VI) residual concentration may be noticed with increasing the peat dose from 4 to 20 g/L (even at 8 g peat/L, Cr (VI) concentration is below the tolerance limit – NTPA). At the same time, almost half of Cr (VI) was reduced to the less toxic Cr (III). This behaviour is also evident from Figure 4. The sorption percent slightly increases with increasing the peat dose (a larger surface area and more sorption sites), while the reduction percent decreases.

Effect of peat dose

The influence of the peat amount (expressed as the ratio of sorbent mass and solution volume) on the sorption and reduction of Cr (VI) from a solution with an initial concentration of 52 mg/L and pH = 2 is plotted graphically in Figure 3.

Figure 3: Effect of peat dose on the residual concentrations of Cr species: $C_0 = 52$ mg/L, pH = 2, time = 24 h

Figure 4: Effect of peat dose on the removal, reduction and sorption of Cr (VI): $C_0 = 52$ mg/L, pH = 2, time = 24 h

Effect of initial chromium (VI) concentration

The influence of Cr (VI) concentration on chromium (VI) removal from an aqueous solution of pH = 2, using peat, is shown in Figure 5.
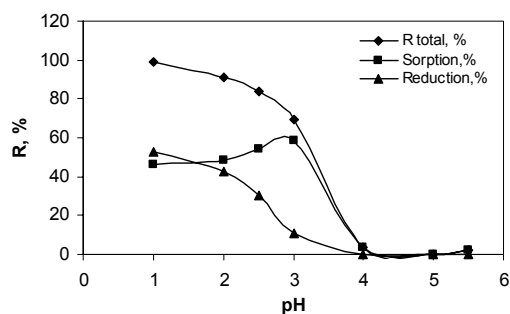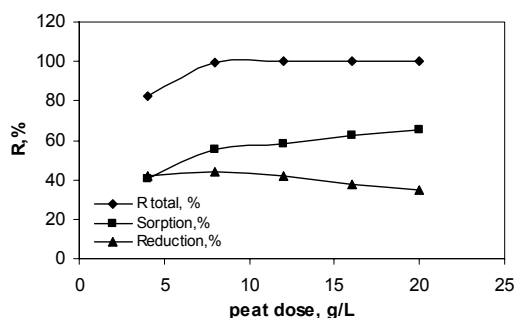
After a 24 h contact time, both Cr (III) and Cr (VI) are present in the residual solution, their concentrations having a growing tendency with increasing the initial Cr (VI) concentration.

However, increasing the initial pH of the solution modifies the chromium species distribution. Thus, at pH = 1-2, the predominant form is Cr (III), while, at pH = 3, residual Cr is present as Cr (VI). The increase in the initial Cr (VI) concentration has no significant effect on the reduction percentage (Fig. 6). At the same time, the sorption percentage decreases, probably due to the saturation of the accessible sorption sites. The higher is the pH, the more intense is the effect.

Effect of contact time

The variation in the residual concentrations of chromium species as a function of the contact time between peat and the solution with an initial concentration of 52 mg Cr/L and pH = 2 is illustrated in Figure 7.

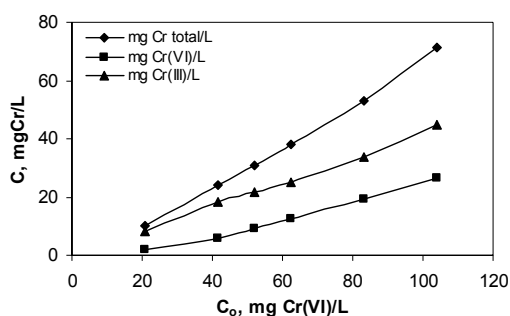As the contact time increases, a slow decrease may be observed in the residual concentration of chromium. After 4 h of contact, the total Cr concentration was of 35.88 mg/L (the values of Cr concentration after 24 h were of 31.34 mg/L, lower by 12.65% than those obtained after 4 h of contact). Also, a permanent change may be noticed in the ratio of Cr (III) and Cr (VI) concentrations: Cr (VI) concentration decreases (down to 9.64 mg/L after 24 h) and, simultaneously, Cr (III) concentration increases (up to 21.7 mg/L after 24 h). In the first 2 h, the rate of reduction is higher than that of sorption; after that both processes take place at almost the same rate (Fig. 8).

This suggests that sorption is a mass transfer process, controlled by the diffusion of the hydrochromate anions present in the porous structure of peat.

Figure 5: Effect of Cr (VI) initial concentration on the residual concentrations of chromium species: pH = 2, peat dose = 4 g/L, time = 24 h
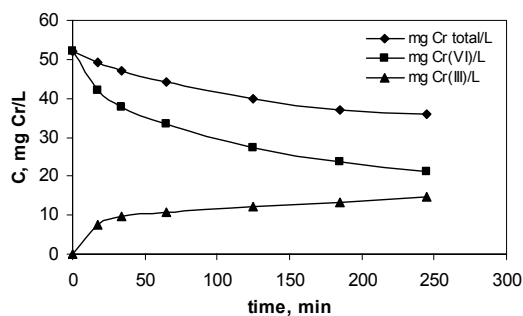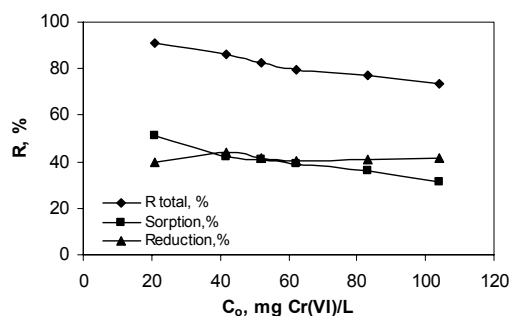

Figure 6: Effect of initial Cr (VI) concentration on removal, reduction and sorption: pH = 2, peat dose = 4 g/L, time = 24 h

Figure 7: Effect of contact time on the residual concentrations of chromium species: pH = 2, C_0 = 52 mg/L, peat dose = 4 g/L
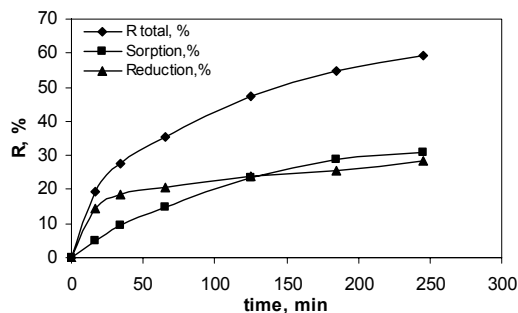

Figure 8: Effect of contact time on the removal, sorption and reduction of Cr (VI): pH = 2, C_0 = 52 mg/L, peat dose = 4 g/L

CONCLUSIONS

The removal of hexavalent chromium from acidic solutions (pH = 1-3), by using Romanian *sphagnum* moss peat, occurs by a combined mechanism: the anionic sorption of $HCrO_4^-$ on peat and the reduction of Cr

(VI) to the less toxic Cr (III). The sorption and reduction are strongly dependent on the solution pH; the Cr (VI) removal efficiency is the highest in solutions of pH = 1-2. The increase in the peat dose (over 8 g/L) assures a complete removal of Cr (VI) from

solutions with a concentration of 50 mg Cr/L and pH = 2. The increase in Cr (VI) concentration slightly decreases the sorption percentage. Both sorption and reduction are dependent on the contact time and the equilibrium attained after 24 h. The results of the present study show that Romanian *sphagnum* moss peat, an available natural and cheap material, can be used as a sorbent and reductant for the removal of chromium (VI) from aqueous waste solutions.

REFERENCES

[1] J. Kotas and Z. Stasicka, *Environ. Pollut.*, **107**, 263 (2000).

[2] S. Goswami and U. C. Ghosh, *Water SA*, **31**, 597 (2005).

[3] E. Oguz, *Colloids Surf. A*: *Physicochem. Eng. Aspects*, **252**, 121 (2005).

[4] NTPA 001/2002 – Romanian normative sets on the pollutant concentrations in wastewater at release into natural receptors.

[5] J. W. Patterson, "Industrial Wastewater Treatment Technology", Butterworth–Heinemann, London, 2nd ed., 1985, 476 pp.

[6] M. Macoveanu, D. Bilba, N. Bilba, M. Gavrilescu and G. Soreanu, in "Ion Exchange Processes in Environment Protection", Matrix Rom, Bucharest, 2002, pp. 312-317.

[7] A. Agrawal, C. Pal and K. K. Sahu, *J. Hazard. Mater.*, **159**, 458 (2008).

[8] C. A. Kozlowski and W. Walkowiak, *Water Res.*, **36**, 4870 (2002).

[9] D. Mohan and C. U. Pittman Jr., *J. Hazard. Mater.*, **137**, 762 (2006).

[10] N. Daneshvar, D. Salari and S. Aber, *J. Hazard. Mater.*, **94**, 49 (2002).

[11] S. Gupta and B. V. Babu, *Chem. Eng. J.*, (2009) doi:10.1016/j.cej.2009.01.013.

[12] K. Selvaraj, S. Manonmani and S. Pattabhi, *Bioresource Technol.*, **89**, 207 (2003).

[13] J. H. Potgieter, S. S. Potgieter-Vermaak and P. D. Kalibantonga, *Miner. Eng.*, **19**, 463 (2006).

[14] M. X. Loukidou, A. I. Zouboulis, T. D. Karapantsios and K. A. Matis, *Colloids Surf. A*: *Physicochem. Eng. Aspects*, **242**, 93 (2004).

[15] J. Romero-Gonzalez, J. L. Gardea-Torresdey, J. R. Peralta-Videa and E. Rodríguez, *Bioinorg. Chem. Appl.*, **3**, 55 (2005).

[16] D. C. Sharma and C. F. Foster, *Water Res.*, **27**, 201 (1993).

[17] P. A. Brown, S. A. Gill and S. J. Allen, *Water Res.*, **34**, 3907 (2000).

[18] D. Park, Y. S. Yun and J. M. Park, *Ind. Eng. Chem. Res.*, **45**, 2405 (2006).

[19] D. Park, S. R. Lim, Y. S. Yun and J. M. Park, *Chemosphere*, **70**, 298 (2007).

[20] Y. S. Ho, J. F. Porter and G. McKay, *Water Air Soil Poll.*, **141**, 1 (2002).

[21] D. C. K. Ko, J. F. Porter and G. McKay, *Trans. Inst. Chem. Eng.*, **81** B, 73 (2003).

[22] W. Ma and J. M. Tobin, *Biochem. Eng. J.*, **18**, 33 (2004).

[23] A. Kicsi, D. Bilba and M. Macoveanu, *Environmental Engineering Management Journal*, **5**, 19 (2006).

[24] A. Kicsi, D. Bilba and M. Macoveanu, *Environmental Engineering Management Journal*, **6**, 205 (2007).

[25] L. Bulgariu, C. Cojocaru, B. Robu and M. Macoveanu, *Environmental Engineering Management Journal*, **6**, 425 (2007).

[26] C. Balan, D. Bilba and M. Macoveanu, *Environmental Engineering Management Journal*, **7**, 17 (2008).

[27] J. Lakatos, S. D. Brown and C. E. Snape, *Fuel*, **81**, 691 (2002).

[28] B. Silva, H. Figueiredo, I. C. Neves and T. Tavares, *Procs. World Academy of Science, Engineering and Technology*, *PWASET*, **33**, 59 (2008).

[29] D. M. Zhilin, P. Schmitt-Kopplin and I. V. Perminova, *Environ. Chem. Lett.*, **2**, 141 (2004).