Non-living Biomass of Water Hyacinth Roots as a Sorbent for Chromium (III) in Aqueous Solution

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ABSTRAK

Kemampuan biojisim yang tak hidup bagi akar pokok kiambang untuk mangalih Cr(III) telah dikaji di bawah beberapa keadaan seperti kepekatan dan pH yang berbeza, kehadiran ion natrium dan kalsium untuk mensimulasikan keadaan dalam buangan dari kilang kulit. Ion kalsium lebih berkesan daripada ion natrium dalam menghalang pengerapan Cr(III) pada akar pokok kiambang. Kajian kinetik menunjukkan terdapat beberapa mekanisme yang terlibat dalam proses pengerapan tersebut. Data keseimbangan sistem Cr(III) - akar pokok kiambang mematuhi isoterma Langmuir dan ini menunjukkan adanya peliputan eka-lapisan pada bahan penerap.

ABSTRACT

The ability of the non-living biomass of water hyacinth roots, *Eichhornia crassipes,* to remove Cr(III) has been studied at different concentrations, pH levels and in the presence of Na and Ca ions in an attempt to simulate the real conditions of tannery waste. Ca ions exhibited a greater inhibitory effect on the Cr(III) sorption than the Na ions. Kinetic studies showed that more than one mode of sorption was operating in the uptake of Cr(III) by water hyacinth roots. The equilibrium data obeyed Langmuir isotherm for the Cr(III)-water hyacinth root system, implying mono-layer coverage of the sorbent material.

Keywords: water hyacinth roots. sorbent. chromium (III). tannery waste

INTRODUCTION

Chromium occurs in aqueous systems in both the trivalent (Cr(III)) and the hexavalent (Cr(VI)) forms and is widely used in a large number of industries, including metal finishing, inks, dyes, pigments, glass, ceramics and glue. It is also employed in chromium tannery, textile dyeing, and wood preservation. Chromium compounds are also used to inhibit corrosion in boiling waters. Consequently, untreated effluents from industrial inputs could contain a wide range of concentrations of this element. The toxicity of chromium has been documented, and depends on its oxidation state. Cr(VI) is approximately 100 times more toxic than Cr(III) (Forstner and Wittmann 1979) because Cr(VI) is

carcinogenic and mutagenic and is also a strong oxidant (Langard 1983). However, both are undesirable in aqueous environments.

Various treatment processes for the removal or reduction of Cr are available; the most commonly used include reduction and precipitation, ion exchange and adsorption. Activated carbon is costly both to use and to regenerate. Recently we investigated the use of chrome sludge for the removal of Cr(III) (Low *et al.* 1995) and in this paper we report on the use of the non-living biomass of water hyacinth roots, a low cost and easily available material, in the removal of Cr(III) from synthetic solutions.

MATERIALS AND METHODS

Materials

Water hyacinth roots were collected from a pond in the vicinity of Universiti Putra Malaysia. No attempt was made to sort out the maturity of the plants. The roots were cleaned with tap water to remove foreign materials, unhealthy parts of the roots were discarded and the roots were finally rinsed with distilled water. The dry roots were then rinsed with 1 M HNO_3. The acid treated roots were washed with distilled water until the pH of the rinse was near neutral. They were dried at 80°C before being ground to pass through a sieve of 1-mm mesh size. The Fourier transformed infra-red spectrum (KBr) of water hyacinth roots was recorded using Perkin Elmer FT-IR Model 1650 in an attempt to establish the functional groups that may be responsible for binding Cr(III) ions.

Batch Studies

All experiments were carried out in duplicate at room temperature (28 ± 2 °C). Variations of more than 5% were discarded and the experiment repeated. Sorption was measured by equilibrating a known weight of the root with various concentrations of aqueous solutions of Cr(III) for a specific time. At the end of equilibration, the solution was centrifuged at 3000 rpm for 10 min for phase separation. The chromium concentration of the supernatant was determined using an inductively coupled plasma-atomic emission spectrometer (Perkin Elmer P1000). Synthetic solutions were prepared from A.R. grade $Cr(NO_3)_3 \cdot 9H_2O$. The effect of pH on Cr(III) sorption was studied by equilibrating sorption-mixtures at different initial pH values, obtained by the addition of 0.1 M HCl or NaOH before the addition of pre-weighed sorbent.

The effect of initial concentration on the sorption of Cr(III) was studied by varying the concentration of the Cr(III) from 4.31 to 136.78 mg/l at pH 3. In all contact time experiments, the sorption mixture consisted of 1.0 g of root with 500 ml of Cr(III) solution of various initial concentrations at pH 3. It was agitated at 200 rpm at room temperature. Aliquots of solutions were withdrawn and analysed for Cr(III) content. The effect of Na and Ca ions was carried out using various weight ratios of Cr(III) to Na/Ca in contact with a fixed amount of sorbent.

RESULTS AND DISCUSSION

FT-IR Spectrum of Water Hyacinth Roots

The FT-IR spectrum of the ground water hyacinth roots is shown in *Fig. 1*. The most prominent peaks appear to be the hydroxyl groups, 3406 cm⁻¹, with a peak at 1638 cm⁻¹. As no other functional groups are discernible from the spectrum, it is assumed that the binding of Cr(III) on the surface of the roots is likely to involve the hydroxyl groups.
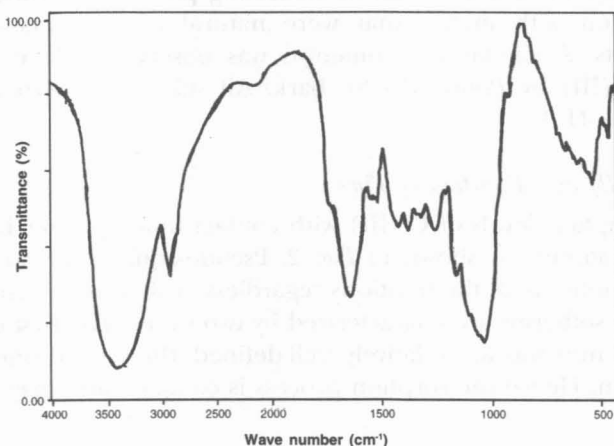

Fig. 1. FT-IR spectrum of water hyacinth root obtained in KBr

Effect of pH on Sorption

The effect of pH on the sorption of Cr(III) by the water hyacinth roots is shown in Table 1. The experiment was limited to pH < 4.5 as Cr(III)

TABLE 1

Effect of pH on the percentage uptake of Cr(III) by water hyacinth roots

pH		Cr(III) uptaken (%)
Initial	Final	
1.80	2.01	0
2.60	3.00	29.9
3.05	3.80	91.2
4.80	5.05	precipitation

Conditions 0.1 g sorbent in 25 ml of 10 mg/l Cr(III) solution. Agitation rate and time: 200 rpm and 3 h respectively

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precipitation occurred above this value. Alves *et al.* (1993) in their study on chromium removal from wastewater 'polishing' by *Pinus sylvestris* bark reported that tests were performed at solution pH < 5 otherwise precipitation of chromium occurred for solutions of concentration of 5-20 mg/l. The effect of pH is important in establishing the optimum sorption of Cr (III) at the liquid/solid interface. At pH 2, there was practically no sorption due to the unfavourable electrostatic repulsion between the positively charged surface and the chromium ions. With the increase of pH from 2 to 3.05, the sorption increased rapidly from 0 to almost 91%. There was a corresponding increase in the final pH of all the solutions, indicating possible exchange of H^+ ions of the solution with metals that were natural constituents of the water hyacinth roots. A similar phenomenon was observed in the study of the uptake of Cr(III) by *Pinus sylvestris* bark. All subsequent experiments were conducted at pH 3.

Uptake of Cr(III) as a Function of Time

Variation of uptake levels of Cr(III) with contact time by water hyacinth roots at room temperature is shown in *Fig. 2*. Pseudo-equilibrium was reached in about 120 minutes in all the solutions regardless of their initial concentrations. The sorption isotherms are characterized by two waves. The first one occurred in the first 20 min and was relatively well-defined; the second one was a slowly rising isotherm. Hence the sorption process is complex and may involve more
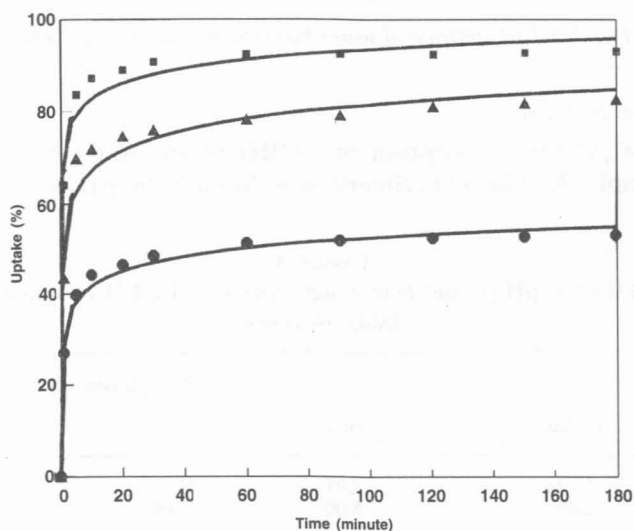

Fig. 2. Sorption of Cr(III) as a function of agitation time; ● - 5 mg/ ▲ - 10 mg/l and ● - 20 mg/l. Conditions: 1.0 g of sorbent in 500 ml of Cr(III) solution of various initial oncentration. Agitation rate: 200 rpm at pH value of 3
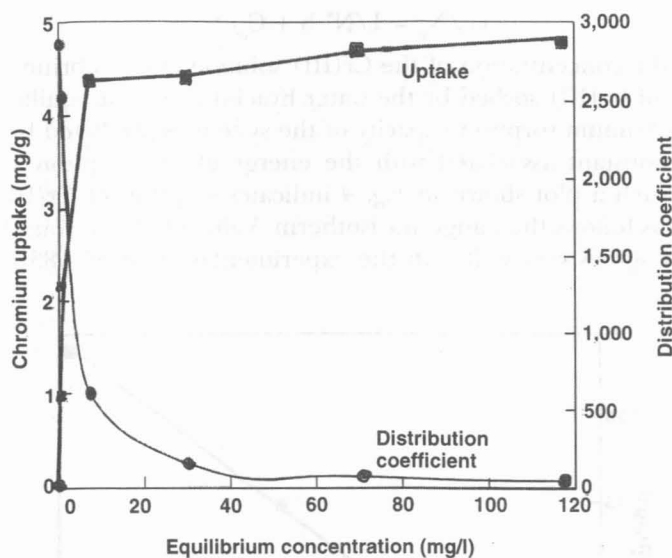
Fig. 3. *Uptake (■) and distribution coefficient (●) of Cr(III) on water hyacinth root. Conditions: 0.1 g of sorbentin 25 ml of Cr(III) solution of various initial concentrations. Agitation rate and quilibration time: 200 rpm and 3 h at pH 3*

than one mechanism. Percentage uptake, which is defined as $\dfrac{\Delta C}{C_i} \times 100$ where $C = C_i - C_t$ where C_i is the initial concentration and C_t the concentration of Cr at time t, follows the usual trend of a greater percentage uptake with decreasing concentration.

Sorption as a Function of Initial Concentration

The roots were treated with solution of initial Cr(III) concentrations of 4.31 to 136.78 mg/l with the final bulk solution concentration varying from 0.35 to 117.39 mg/l. The sorption isotherm, as shown in *Fig. 3* resembles those of other biological materials. The percentage uptake increases with decreasing concentration. The distribution coefficient as defined by [mg Cr(III) per g sorbent]/ [mg Cr(III) per g solution at equilibrium] varies from 2853 to 41 from the least to the most concentrated starting solutions. The large distribution coefficient of the root-Cr(III) system means that the non-living mass of the water hyacinth roots possesses useful separation properties, especially for dilute solution. A plot of chromium uptake (mg Cr/ g sorbent) versus equilibrium concentration shows that sorption increased until all sorption sites were saturated with Cr(III) ions. Extrapolation of the curve provides a maximum sorption of 4.83 mg Cr(III)/g sorbent.

The results from the sorption data obtained after equilibrium were fitted into a modified Langmuir isotherm model of the following form:

$$C_e/N_e = 1/N^* \, b + C_e/N^*$$

where C_e is the concentration of the Cr(III) solution at equilibrium (mg/l), N_e the amount of Cr(III) sorbed by the water hyacinth roots at equilibrium (mg/g), N^* the maximum sorption capacity of the system as predicted by the model and b is a constant associated with the energy of the sorption system. The linearity of such a plot shown in *Fig. 4* indicates sorption of Cr(III) on water hyacinth roots follows the Langmuir isotherm. Value of N^* was found to be 4.77 mg/g which agrees very well with the experimental value of 4.83 mg/g.
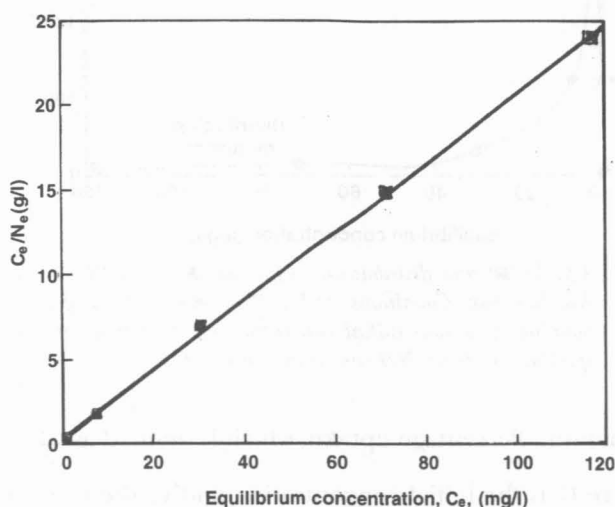

Fig. 4. Langmuir isotherm of Cr(III) sorption on water hyacinth root. Conditions: 0.1 g of water hyacinth roots in 25 ml of various Cr(III) initial concentrations. Agitation rate and time: 200 rpm and 3 h at pH 3

Effect of Sodium and Calcium Ions on Sorption

As the tannery waste contains a large amount of Na and Ca ions, their effect on the Cr(III) -water hyacinth root system was investigated. It has been reported that levels of Na and Ca ions in treated tannery wastewater can attain values of up to 2000 and 300 mg/l respectively (Sengul and Gurel 1993). Other metal ions such as Al, Zn, Cu and Mg appeared to be low. Hence investigation of the effect of Ca and Na ions on Cr(III) sorption using the above modified values was carried out. The results of such a study are shown in Table 2. In the presence of 1000 mg/l of sodium ions the sorption of Cr(III) was inhibited by 15.1% . This is probably due to the steric hindrance of sodium ions preventing Cr(III) ions access to the binding sites of the water hyacinth roots. Calcium ions exhibit a greater inhibitory effect on the Cr(III) sorption as seen by the reduction of Cr(III) sorption by 17.3% in the presence of 100 mg/l of Ca ions. Hence experimental data obtained from the study of pure Cr(III) solution has

TABLE 2

Effect of sodium and calcium ions on the sorption of
Cr(III) by water hyacinth roots

Ca(mb/L)	Na(mg/l	CrUptaken
0	0	70.1
0	100	67.6
0	1000	55.0
10	0	67.9
50	0	57.9
100	0	52.8
100	1000	34.4

Condition: 0.1g of sorbent in 25ml of 25 mg/l Cr(III)
solution. Equilibration time: 3 h, agitation rate: 200 rpm
at room temperature at solution pH 3.

to be interpreted with caution when it is applied to a real sample, especially
when the presence of other ions is suspected.

Effect of Agitation Rate

The effect of agitation rate on the uptake of Cr(III) by water hyacinth roots is
shown in *Fig. 5*. Increasing agitation rate increases the external film mass
transfer coefficient and hence the rate of uptake. This is due to the reduction
of the film boundary layer surrounding the sorbent particles. However in our
present study there is very little difference in the sorption curves at agitation
rates of 10, 100 and 200 rpm, the higher rate giving slightly higher sorption.
According to McKay (1982), the sorption process could involve four distinct
steps: (i) migration of sorbate molecules to the sorbent surface from solution
(ii) diffusion through the boundary to the surface of sorbent (iii) sorption at
binding sites and (iv) intraparticle diffusion into the interior of the sorbent. At
an agitation rate of 10 rpm there was sufficient energy to overcome the
boundary layer effect. This is borne out by the time course curves in *Fig. 5* . In
a system where the agitation of solid-solution is vigorous, intraparticle diffusion
is likely to be the limiting step. This possibility was examined in terms of a
graphical relationship between amount of Cr(III) sorbed, q_t (mg/g) and the
square root of agitation time t (min) in the relation of $t^{0.5} K_d = q_t$ (Jayson *et al.*
1993). Such plots are shown in *Fig. 6*. All the graphs show similar features; an
initial curve followed by a straight line, this indicates that more than one mode
of sorption was operating in the sorption of Cr(III) by water hyacinth roots.
The initial curve is due to boundary layer diffusion while the linear portion can
be attributed to intraparticle diffusion. The rate constants for the intraparticle
diffusion, K_d, determined from the slopes of the linear portions are
5.24×10^{-2}, 7.58×10^{-2} and 12.99×10^{-2} mg/g^{-1} min$^{-1/2}$ for Cr(III) solutions of 5,
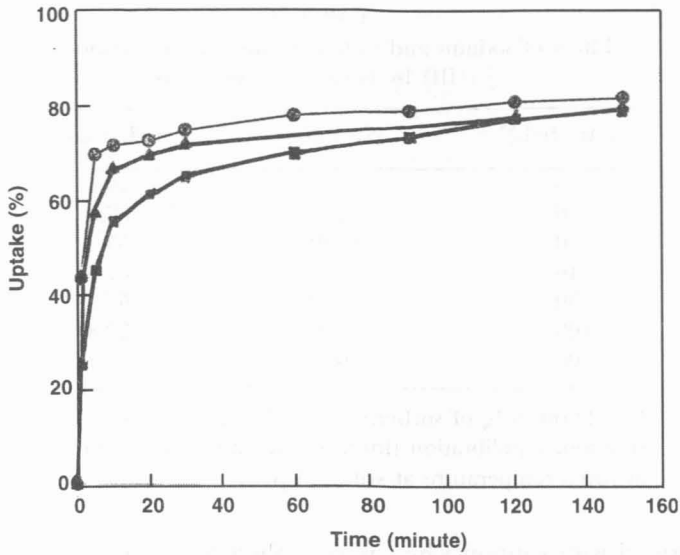10 and 20 mg/l respectively. As the lines do not pass through the origin, it

Fig. 5. *Effect of agitation rate on the sorption of Cr(III) by water hyacinth root; ● - 10 rpm, ▲ - 100 rpm and ● - 200 rpm. Conditions: 1.0 g of sorbent in 500 ml of 10 mg/l Cr(III) solution at pH 3*
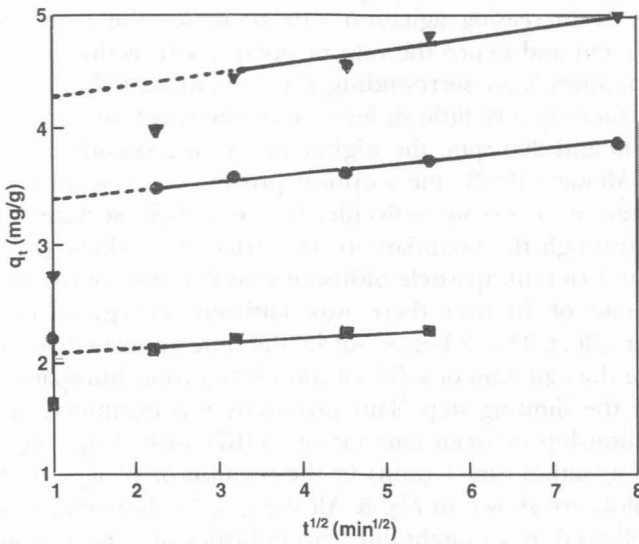

Fig. 6. *Plots of amount sorbed as a function of $t^{1/2}$ for the intraparticle transport of Cr(III) on water hyacinth root at room temperature at pH 3; ■ - 5 mg/l, ● - 10 mg/l and ▼ - 20 mg/l*

appears that particle diffusion is not the only rate-controlling step in the sorption of Cr(III) by water hyacinth roots (Singh *et al.* 1988).

CONCLUSION

The non-living biomass of water hyacinth roots, an easily available bio-material, has been shown to have the ability to remove/reduce Cr(III) from synthetic solution and tannery waste. The roots offer several advantages over living plants. It can be stored easily and there is no associated problems of maintaining living plants. The material can be used as a source of fuel if regeneration is not desired.

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