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Chromium(III) Sorption Enhancement Through NTA—Modification of Biological Materials

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The use of low-cost biological materials for the removal and recovery of heavy metals from solution has been investigated extensively in recent times. To enhance their sorption capacities various chemical modifications on the sorbents were attempted. Freer *et al.* (1989) showed that bark from the *Pinus radiata* (D. Don) had a greater sorption capacity for metals after treatment with both inorganic acid and formaldehyde. Apple wastes treated with phosphorus oxychloride improved the efficiency of removing metal ions (Maranon and Sastre 1992). Ethylenediamine tetraacetic acid (EDTA)-modified groundnut, *Arachis hypogea,* was reported to improve the sorption of cadmium and lead ions (Okieimen *et al. 1991).* Modifications with the aid of dyes also enhanced metal sorption (Suemitsu *et al.* 1986; Shukla and Sakhardande 1991; Low *et al.* 1993, 1995).

Moss and coconut husk (CH) are readily obtainable in Malaysia. Their sorption potential for metals has been reported (Low and Lee 1991; Low *et al.* 1995). In this paper we report on the metal sorption enhancement of these two biosorbents after chemical modification with nitrilotriacetic acid (NTA).

MATERIALS AND METHODS

The collection and preparation of moss and coconut husk have been described elsewhere (Lee and Low 1989; Low *et al. 1995).* Samples of the moss and coconut husk, in their natural states, were dried at 80° C overnight. The dried biosorbents were ground and sieved to pass through a 1- mm sieve. The material was acidified with sulfuric acid for 2 hr. The mixture was then washed thoroughly with distilled water and dried at 80° C. The acid -treated material was treated with a mixture of NaOH and NTA at 70° C for 3 hr. The reaction mixture was then washed with distilled water until the pH of the filtrate was near neutral. It was

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then dried before experimentation. The NTA-modified biosorbents were labeled as NTA-moss and NTA-CH for the treated moss and coconut husk, respectively.

Tannery wastewater was obtained from a local tannery factory located in Jalan Klang Lama, Kuala Lumpur.

The sorption capacities of the NTA-modified moss and NTA-CH were compared with those which were modified by acid, alkali, formaldehyde, (Kumar and Dara 1982) , phosphorus oxychloride (Maranon and Sastre 1992) and EDTA (Okieimen *et al. 1985).*

The effect of pH on metal sorption was investigated by equilibrating the sorbate-sorbent mixture at different initial pH values by the addition of 0.1 *M* HCl or NaOH before the addition of pre-weighed sorbent.

All sorption measurements were carried out by agitating a known weight of sorbent with various aqueous solutions of the metal ions at 100 rpm at room temperature for a specified time. The sorbent-solution mixture was then filtered and the concentration of the metal ions was determined using an inductively coupled plasma-atomic emission spectrometer (Perkin Elmer P10000).

In order to establish the maximum sorption capacities for the NTA-modified and the unmodified moss and CH, the effect of initial concentration on the sorption of metal ions on the various sorbents was studied by varying the initial metal concentration with a constant weight of sorbent.

RESULTS AND DISCUSSION

The ability of the various chemically-modified forms of moss and coconut husk to sorb Cr(III) is shown in Figure 1. Chemical modifications through NTA and EDTA showed enhanced sorption for Cr(III) in aqueous solution in both biological materials. Treatment with H_2SO_4, $POCl_3$ and HCHO gave lower sorption performance. The order of Cr(III) sorption for both the materials follows the order of the following treatments: NTA>EDTA>natural, NaOH>H_2SO_4, HCHO>$POCl_3$. As NTA-modified moss and coconut husk gave the best sorption performance, all subsequent experiments were carried out using these materials.

The study on the sorption of Cr(III) by NTA-moss and NTA-CH as a function of pH is shown in Figure 2. The pH value of the solution determines the amount of free metal ion from bound chemical forms and it also controls the sorption of the metal ions at the interface of the sorbent-solution system. The sorption increased with increasing pH for both

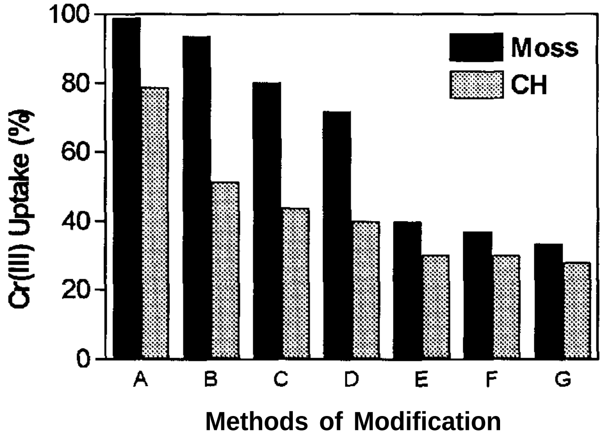

Figure 1. Uptake of Cr(lll) by different chemically-modified forms of moss and coconut husk. Conditions: 0.1 g sorbent in 25 mL of 1.92 m*M* Cr(lll) solution (pH - 4.50) at 100 rpm for 2 hr. A - NTA; B - EDTA; C - natural ; D - NaOH; E - H_2SO_4; F - HCHO and G - $POCl_3$.

modified and natural biological materials. NTA-moss had a greater uptake ability at all levels of pH compared to NTA-CH. Precipitation occurred at pH>5 and since this study was concerned with sorption and not precipitation, all experiments were performed at pH<5. The sorption capacity of the materials follows the order of NTA-moss>NTA-CH, moss> coconut husk. The sorption enhancement of NTA is probably due to the greater carboxylic groups per unit of NTA which was bound to the surface of the biosorbents.

At low pH, the surface of the sorbents was surrounded by H^+ ions which would either hinder the approach of Cr(lll) ions from reaching the binding sites of the sorbents or making sorption unfavorable through repulsion. A similar observation was also reported by Low and Lee (1991) in the study of uptake of Cd by moss and Kumar and Dara (1982) in the removal of metal ions by treated peanut skin.

The rates of Cr(lll) uptake by the modified biosorbents are shown in Figure 3. The percent uptake , defined as 10O(C_i - C_t)/C_t, where C_i and C_t are the concentrations of the Cr(lll) solutions at time 0 and t, respectively, shows rapid uptake at the initial stage of sorption followed by a slowly rising isotherm. Hence, the sorption process could be complex and might have involved more than one mechanism. Pseudo-equilibrium was achieved in about 60 minutes. The rapid uptake of Cr(lll) by the biosorbents indicates that they could be useful in column study where the contact time between the sorbate and sorbent is generally short. The rapid uptake could be due to the ion-exchange between the metal cations and the negatively charged binding sites of the sorbents. A similar

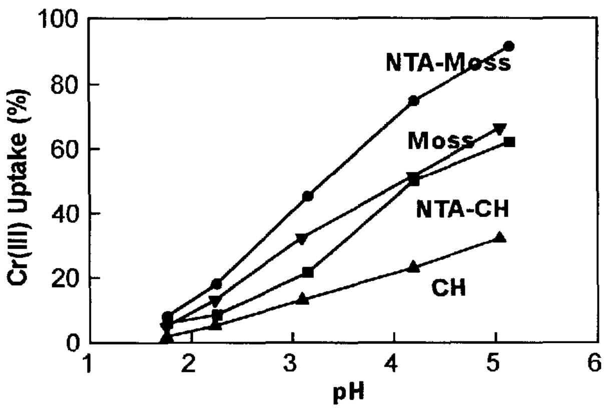

Figure 2. Effect of pH on the sorption of Cr(III) by different sorbents. Conditions: 0.1 g sorbent in 25 mL of 3.15 m*M* Cr(III) solution at 100 rpm for 2 hr.

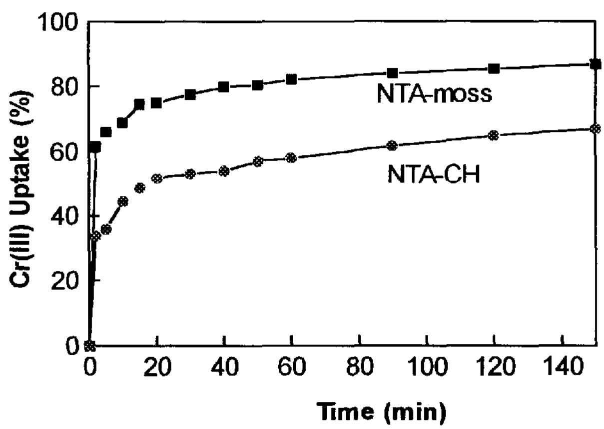

Figure 3. The rate of Cr(III) uptake by NTA-moss and NTA-CH. Conditions: 0.1 g sorbent in 25 mL 3.15 m*M* Cr(III) solution (pH - 4.50) at 100 rpm at room temperature.

observation was also noted in the uptake of copper by dye-treated oil palm fibres (Low *et al. 1993).*

The distribution of Cr(III) between the sorbent and the solution, when the system is in a state of equilibrium, is important in establishing the sorption capacity of the sorbent for Cr(III). The general sorption isotherms that can be used to describe the sorption of Cr(III) include Langmuir, Freundlich and BET (Brauner-Emmett-Teller). The sorption data from the uptake at various initial Cr(III) concentrations by various biosorbents were

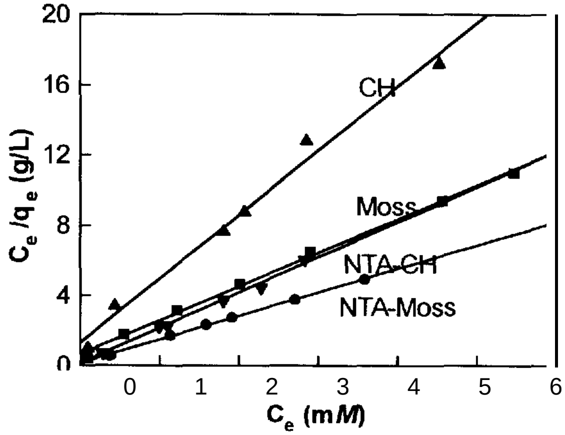

Figure 4. **Langmuir isotherms for the sorption of Cr(III) by various sorbents at room temperature.**

fitted into Langmuir isotherm of the following form: $C_e/q_e = 1/N^*b + C_e/N^*$ where C_e is the equilibrium concentration (m*M*), q_e the amount of Cr(III) sorbed at equilibrium (mmol/g), N^* , maximum sorption capacity(mmol/g) and b, a Langmuir constant related to the energy of sorption. Linear plots (Fig. 4) of C_e/q_e versus C_e yielded straight lines indicating the validity of applying Langmuir isotherm model on the present sorption process. The value of N^* and the enhancement factor, defined as $100(N^*_{NTA} - N^*)/N^*$, are shown in Table 1. NTA modification on both moss and coconut husk gave 44 and 79% increase in sorption capacity, respectively.

Table 1. Langmuir constant and enhancement factor for Cr(III) - sorbent systems.

Sorbents	N^*(mmol/g)	Enhancement factor (%)
Moss	0.52	
NTA-moss	0.75	44
Coconut husk	0.28	
NTA-coconut husk	0.50	79

The uptake of Cr(III) in the presence of other metal ions would be expected to be reduced as the binding sites of the sorbents are finite.

The competitiveness of various ions in a mixed solution when treated by the modified sorbents is shown in Figure 5. The order of sorption for both the modified sorbents is Pb>Cr(III)>Cu>Ag> Cd>Zn. The amount sorbed depends on the ionic potential, radius, charge, hydrolysis and also the electro-chemical properties of the metal ions (Mattuschka and Straube 1993).

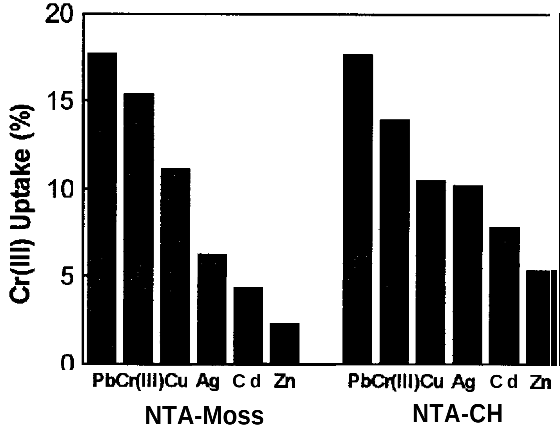

Figure 5. Sorption of Cr(III) by NTA-moss and NTA-CH in the presence of other ions. Conditions :0.2 g of sorbent in 50 mL of 3.15 m*M* Cr(III) solution (pH - 3.14) at 100 rpm for 2 hr.

Table 2. Uptake of Cr(III) by various sorbents from tannery waste. Conditions: 0.1 g sorbent in 25 mL 3.15 m*M* Cr(III) tannery waste (pH - 4.50) at 100 rpm for 2 hr.

Sorbents	Cr(III) Uptake (%)
Moss	32.1
NTA-Moss	54.9
Coconut husk	9.9
NTA-Coconut husk	35.2

The effectiveness of the sorbents in removing Cr(III) from tannery waste is shown in Table 2. Sorption of Cr(III) was lower than that in synthetic solution . This was due to the presence of other ions such as Na^{+} and Ca^{2+} in the tannery waste which interfered with the binding of Cr(III) ions (Alves *et al*. 1993). Although the uptake of Cr(III) was reduced in the tannery waste, the order of sorption for the four sorbents remained the same as that with synthetic solution.

This preliminary study showed that modification of moss and coconut husk through NTA enhanced the sorption of Cr(III) from aqueous solution by about 50% suggesting that these materials could be employed in the removal/reduction of Cr(III) from tannery waste.

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