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Binding of Iron, Zinc, and Lead Ions from Aqueous Solution by Shea Butter (*Butyrospermun Parkii*) Seed Husks

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Several workers have reported on the potential use of agricultural products as substrates for the removal of metal ions from aqueous solutions (Roberts and Rowland 1973; Kumar and Dara 1981; Okieimen et al. 1985, 1986, 1988; Okieimen and Okundaye 1989). These studies demonstrated that considerable amounts of metal ions can be removed from aqueous solutions by cellulosic materials. The merit in the use of the latter is their relative abundance and cheapness compared to conventional materials for the removal of toxic metal ions from waste-waters. In some of the studies, chemical modification of cellulosic materials significantly enhanced their ion-binding properties, providing greater flexibility in their applications to a wide range of heavy metal ions.

Shea butter plant (Butyrospermun Parkii) normally grows in the wild within the guinea-savana zone of Nigeria. The seeds are a rich source of edible oils and the husks are usually discarded. The husk is thus available in abundance and, hence, there is reason to examine its ion-binding properties for its possible application in the removal of toxic metal ions from industrial waste-waters. This paper reports on preliminary studies of the sorption of iron, zinc and lead ions from aqueous solution by modified and unmodified shea butter seed husks.

MATERIALS AND METHODS

Shea butter seeds were collected from a local farm by the Federal University of Technology, Yola. The husks were removed, washed with deionized water and dried. The husks were then ground to fine size, sieved through a 300-um mesh screen and dried again at 40°C. The portion of the seed husks retained on the sieve was divided into three parts; one part of the husks was used for sorption studies without chemical modification and the others were modified by the introduction of EDTA and thiol groups. The seed husk was EDTA - modified by the method reported by Okieimen and Orhorhoro (1986). A 30-gram sample of seed husks was hydrolyzed with 500 ml of 7% (v/v) aqueous sulphuric acid for 24 hr at 65°C.

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The mixture was filtered, the seed husk washed with deionized water several times and then dried at 50°C. Seventeen grams of the hydrolyzed product were refluxed in a mixture of 300 ml of pyridine and 56.7 g of EDTA for 3 hr at 70°C. The mixture was cooled, followed by addition of 300 ml of deionized water and then filtered. The filtered product (EDTA - modified) was washed copiously with deionized water and dried at 50°C for 24 hr.

The seed husk was thiolated by the method of Okieimen and Okundaye (1989). Specifically, a 25-gram sample of the powdered seed husks was thiolated with 250 ml of 1.0 M solution of thioglycolic acid for 24 hr at 29°C (Okieimen and Okundaye 1989). The mixture was filtered, washed with deionized water and then with methanol. It was finally washed with deionized water and dried at 50°C. The degree of thiolation was estimated titrimetrically by reaction of the thiolated husk with iodine and back-titration of the unreacted iodine with sodium thiosulphate solution.

Studies on sorption of metallic ions from aqueous salt solution by the modified and unmodified seed husks were conducted by the introduction of a 2-gram sample of the seed husk into 100 ml of the metal ion solution of a known concentration (Okieimen and Orhorhoro 1986). At the end of a given time, the husks were removed from the mixture by rapid filtration and the metal ion concentration in the filterate was determined by atomic absorption spectrometry.

RESULTS AND DISCUSSION

The sorption of Zn(II) ion from aqueous solution by unmodified shea butter seed husks at different initial metal ion concentrations is presented in Figure 1. Sorption increased with contact time over the period of 5 to 60 min for each initial metal ion concentration. In addition, the amount of ion sorbed increased with the initial metal ion concentration, which ranged between 300 and 600 ppm. For the 600 ppm initial concentration, the equilibrium concentration of Zn(II) ion sorbed was 13.4 mg/g of sorbent, representing about a 7-fold increase over the equilibrium value at 300 ppm. Figure 2 shows the sorption of Zn(II), Fe(II) and Pb(II) ions by the unmodified seed husk at the initial concentration of 600 ppm of metal ion at 30°C. For each of the metal ions, the amount sorbed also increased with contact time. More Zn(II) ion was removed than either Fe(II) and Pb(II) ions, i.e, the values are in the order Zn(II) > Fe(II) > Pb(II), corresponding to 13.4 mg/g, 10.00 mg/g and 7.0 mg/g sorbent, respectively. Differential adsorption of metal ions from solutions by an adsorbate has been generally ascribed to (1), differences in ionic radii of the metal ions, (2) differences in the affinity of the metal ions for active groups on the adsorbate and (3) nature of the anions of the salt of the metal ion. Clearly, the order of the equilibrium concentrations of the metal ions sorbed was not consistent with

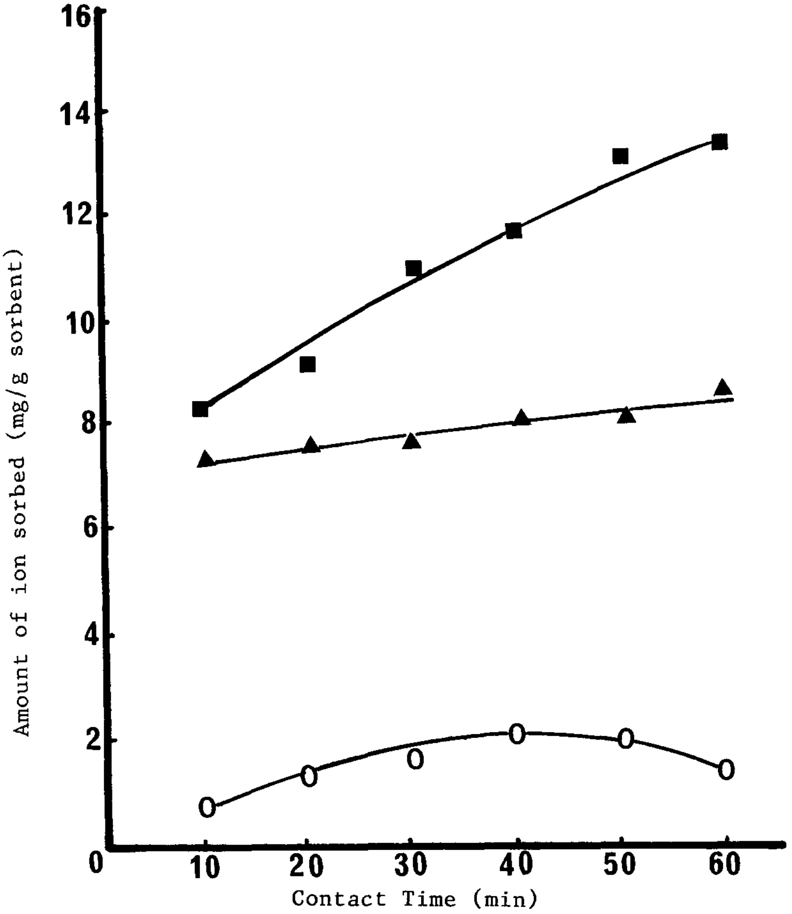

Figure 1: Sorption of Zn(II) ions by unmodified shea butter seed husks at 30°C: initial metal ion concentration, (O), 300 ppm; (▲), 400 ppm (■), 600 ppm

any one of the factors mentioned above,suggesting that the adsorption process is complex. However, for Pb(II) and Fe(II) the equilibrium concentrations are in the order consistent with the order of their ionic radii, i.e, 0.84 nm and 0.64 nm, respectively. The amount of Pb(II) uptake by the unmodified shea seed husk is comparable to the value reported for unmodified groundnut husk (Okieimen et al. 1985). It is, however, significantly more effective in binding Pb(II) than melon seed husk (Okieimen et al.1986).

The rate at which equilibrium is attained may be either film-diffusion controlled or particle-diffusion controlled. Based on the concept of a linear driving force (Chanda et al. 1983), the following relationship holds for the particle-diffusion controlled sorption processes, i.e, $\ln(1-\alpha)=-kpt$ where α is the fractional attainment of sorption equilibrium. α is

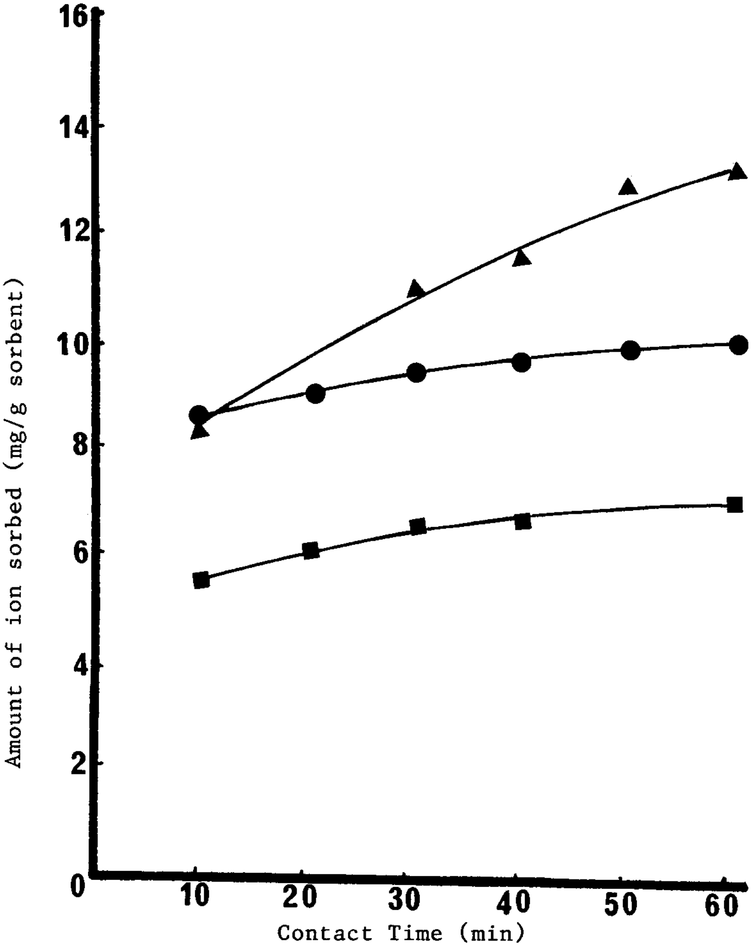

Figure 2: Sorption of Zn(II), (▲), Fe(II) (●), and Pb(II) (■) ions by unmodified shea butter seed husks at 30°C: initial metal ion concentration, 600 ppm.

calculated from x/x* (Okieimen and Okundaye 1989) where x is the amount of metal ion sorbed by a unit mass of the sorbent at time t and x* is the amount of metal ion sorbed when equilibrium is attained. kp is the rate coefficient for the particle-diffusion controlled sorption processes. Figure 3 presents a semi-logarithmic plot of $(1-\alpha)$ versus t for sorption of Zn(II), Fe(II) and Pb(II) by unmodified seed husk. The values for kp derived from the plot for Zn(II), Fe(II) and Pb(II) are 0.0895 min^{-1}, 0.0546 min^{-1}, and 0.0543 min^{-1}, respectively. Thus it can be seen that the rates of attainment of equilibrium for Fe(II) and Pb(II) are comparable but are significantly lower than the value for Zn(II).

Sorption of Pb(II) ion by modified shea butter seed husks is presented in Fig.4. The metal ion uptake increased with contact

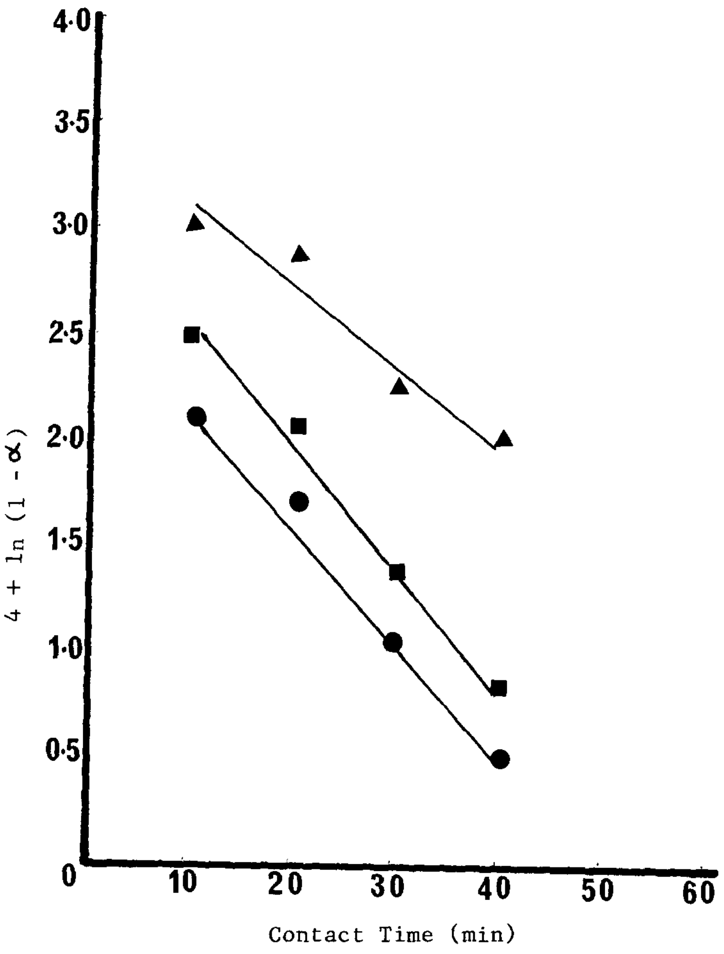

Figure 3: Sorption of Zn(II) (▲), Fe(II) (●), and Pb(II) (■), ions by unmodified shea butter seed husks at 30°C under particle-diffusion control.

time for both EDTA-modified and the thiolated seed husks. Furthermore, EDTA modification increased the equilibrium sorption by 70% over the value for the unmodified husks, but was lower than the equilibrium sorption value for the thiolated seed husk. The equilibrium sorption of Pb(II) ion by the thiolated seed husks was 21.0 mg/g sorbent, representing an increase of about 75% over the value for the EDTA-modified seed husks. A quantitative estimation of the rate of adsorption of Pb(II) by the modified and unmodified husks was derived by a plot of lnCo/C versus t as shown in Fig.5. The half-times for the removal of Pb(II) from aqueous solution at 30°C are shown in Table 1. The values clearly show that the removal of Pb(II) ion from solution is faster with the thiolated husk than with the EDTA-modified husk by a factor of five. The half-time of Pb(II) uptake by the EDTA-modified shea butter seed husks is comparable to

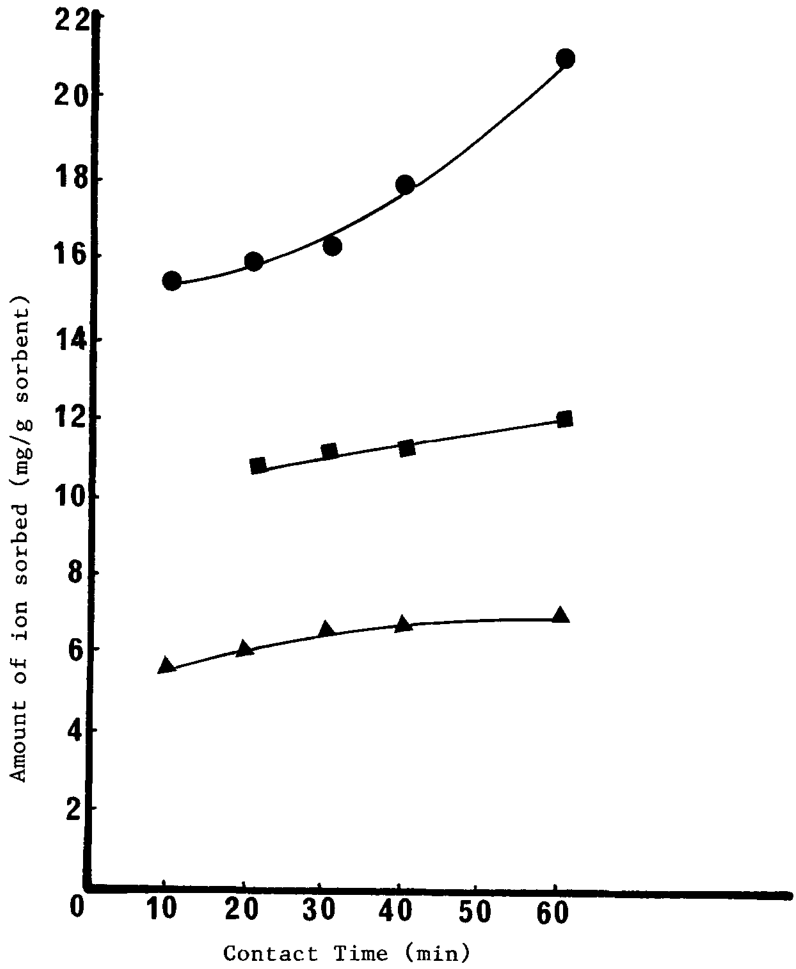

Figure 4: Sorption of Pb(II) ion by shea butter seed husks at 30°C: initial metal ion concentration, 600 ppm. Thiolated husk, (●): EDTA-modified husk (■); unmodified husk, (▲)

the value for Cd(II) uptake at 29°C by EDTA-modified maize stalk, i.e, 364.79 min (Okieimen and Orhorhoro 1986). The results from this study show that shea butter seed husks are effective for the removal of heavy metal ions from aqueous solutions. For adsorption of Pb(II) ion, the unmodified shea butter seed husks appear to be more effective than melon seed husks. Thus, shea butter seed husks may be used for removal of heavy metal ions from waste-waters.

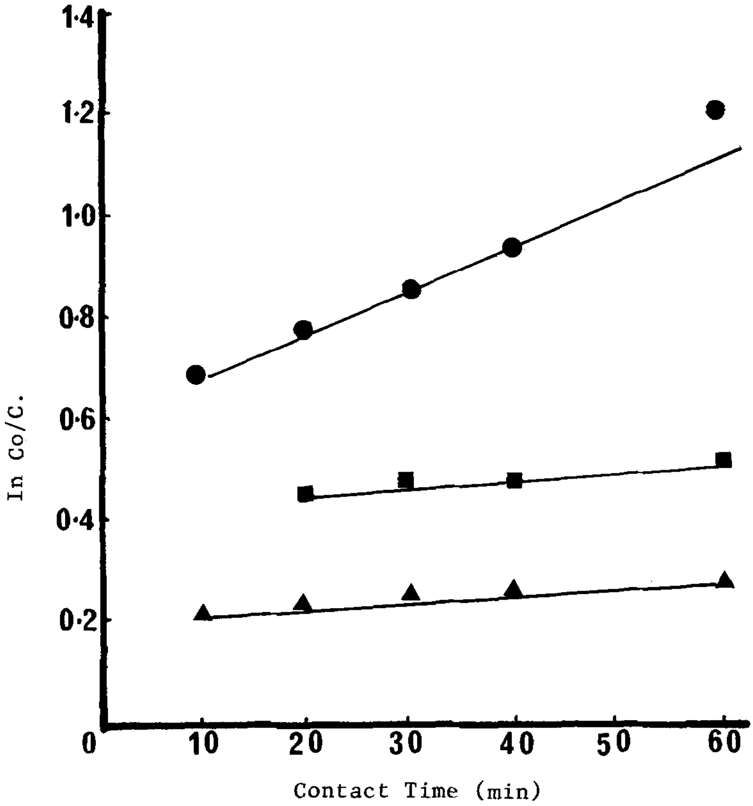

Figure 5: Rate of sorption of Pb(II) ion from 600 ppm solution at 30°C. Thiolated husk, (●); EDTA-modified husk (■); unmodified husk (▲).

Table 1. Rate of Pb(II) uptake by modified shea butter seed husk at 30°C.

Shea butter seed husk	10^3xk min^{-1}	$t_{\frac{1}{2}}$ min
Thiolated	8.6	80.58
EDTA-modified	1.8	385
Unmodified	1.4	495

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