Pertanika J. Sci. & Technol. 1(2): 179-184 (1993)
ISSN: 0128-7680

Removal of Chromium (III) from Aqueous Solution by Coconut Husk and Rice Straw

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Received 29 January 1992

ABSTRAK

Sabut kelapa dan sekam padi didapati boleh mengasingkan dengan banyak ion-ion chromium (III) dari larutan akuas. Pengasingan ion logam adalah fungsi kepada pH dan kepekatan. Julat pH optimum bagi pengambilan Cr (III) ialah 4-6 untuk kedua-dua substrat. Muatan penjerapan sabut kelapa dan sekam padi terhadap Cr (III) ialah masing masing 0.55 dan 0.30 milimol/g substrat. Kajian kinetik penjerapan menunjukkan proses pengasingan mengikut ekspresi kadar tertib pertama. 'Keluk-keluk munculan' dan efisiensi penjerapan berbagai kolum yang mengandungi media campuran sabut kelapa/sekam padi, tanah pasir telah dihasilkan. Keputusan ini menunjukkan sisa pertanian tersebut boleh digunakan sebagai halangan di dalam "landfill" unutk memaksimumkan ketakgerakan ion logam toksik seperti Cr (III) di dalam "leachate".

ABSTRACT

Coconut husk fibre and rice straw were found to be able to remove significant amount of Cr (III) ions from aqueous solutions. Its removal is a function of pH and concentration. The optimum pH range for maximum uptake is between 4 and 6 for both substrates. The adsorption capacity was found to be 0.55 and 0.30 millimole Cr (III)/g substrate for coconut husk and rice straw respectively. The adsorption kinetic studies show that the removal process follows a first order rate expression. The breakthrough curves and adsorption efficiency of various columns containing mixed media of coconut husk/rice straw, soil and sand have been obtained. The results demonstrate that these agricultural residues could be used as barriers in a landfill to maximize immobilization of toxic metal ions such as Cr (III) in leachates.

Keywords: pH, equilibrium time, adsorption capacity, breakthrough curves.

INTRODUCTION

Many recent papers have reported the use of agricultural residues such as sawdust (Srivastava *et al.* 1986), barley straw (Larsen and Schierup 1981), rice straw (Tan *et al.* 1988), waste tea leaves (Tan and Khan 1988) and coconut husk (Tan 1986) for the removal of toxic metal ions from wastewater.

As a continuation of our previous work in this area (Tan 1986; Tan and Khan 1988; Tan *et al.* 1988) we would like to report the use of coconut husk fibres (CH) and rice straw (RS) for the removal of the chromium (III) ion from solution. Trivalent chromium is hazardous to health if ingested excessively.

The use of coconut husk and rice straw as barriers in landfill to maximize immobilization of toxic metal ions in leachates has also been considered. This may reduce the cost of leachate treatment especially where recycling of leachate is employed (Tan *et al.* 1988).

MATERIALS AND METHODS

The Preparation and Treatment of Coconut Husk and Rice Straw

Substrates were ground using a grinder, model FFC-23A. They were sieved using the successful sieving method. Substrates with size range of 0.3 to 0.85 mm were used. They were boiled in distilled water for 1/2 hour to remove the colour followed by treating them with 1.5 M NaOH and 2M HNO_3. Distilled water was used to remove excess base or acid. The substrates were dried in the oven at 100°C overnight before use.

Soil and Sand

The soil samples used in this study were collected from a farm in Universiti Pertanian Malaysia, Serdang. They were subjected to the same treatment as mentioned above. The soil samples used contained 71.5% sand, 26.7% clay and 0.1% organic matter. Fine white quartz sand of high purity containing essentially no organic matter was used as control in the column study.

Reagent and Apparatus

Analar grade chromium (III) chloride hexahydrate ($CrCl_3 . 6H_20$) was used to prepare metal ion solution with double distilled water. The Cr (III) content was analyzed using a flame atomic absorption spectrophotometer (Model IL 651). The samples collected were stored in acid-washed polyethylene bottles before analysis.

Batch Tests

The adsorption kinetic experiment was performed by adding 2.0 g rice straw to 800 ml of Cr (III) solution containing 25 μg/ml of chromium (III) ions. The solution was adjusted to a pH of 4.45 with 0.001 M acetate buffer. Continuous mixing was provided by a magnetic stirrer. Suspensions (3 ml) were withdrawn at 10-minute intervals for two and a half hours for metal analysis. The total volume of suspensions withdrawn was about 6% of the reacting mixture.

The effect of pH on the Cr (III) uptake capacity was tested by adding 400 mg of rice straw or coconut husk to 50 ml of 20 μg/ml Cr (III) solution in a 100 ml polyethylene bottle for various pH values. The mixtures were shaken for 2 hours. The adsorbates were isolated by decantation or filtration (when necessary) and analysed for Cr (III). The pH of the solutions was adjusted by 0.005M CH_3 $COONa/CH_3COOH$ buffer in 0.01 M $KN0_3$. The relationship between the initial Cr (III) concentration and metal ion uptake was studied by mixing 50 mg of the substrate with Cr (III) solutions ranging from 0-60 mg/1 and 2-45 mg/1 for coconut husk and rice straw respectively at pH 4.54. The metal ion in equilibrium was measured after the mixtures were shaken for two hours.

Column Studies

Polyethylene columns of 2.15 cm internal diameter and 14 cm height were used. Flow rates were regulated by a valve. In the study of breakthrough curves for mixed substrates, the columns were packed with 1.7 cm of substrate at the top layer (a) and 10.3 cm of either soil or sand at the bottom layer (b).

RESULTS AND DISCUSSION

Batch Tests

pH Effect

The effect of pH on the uptake of 20 μg/ml Cr (III) by 0.40 gm substrates is shown in *Fig. 1*. It is evident that the chromium (III) ion uptake is pH-dependent. The optimum pH range exceeding 93% uptake is between 4 and 6 for both coconut husk and rice straw. Cation exchange and/or specific ion adsorption were thought to be the mechanism(s) for the metal ion uptake. Below pH 3, desorption of metal ion begins to take place. In the desorption studies, 0.1 to 1.5 M HCl and 0.5 to 1.5 M HCl were found

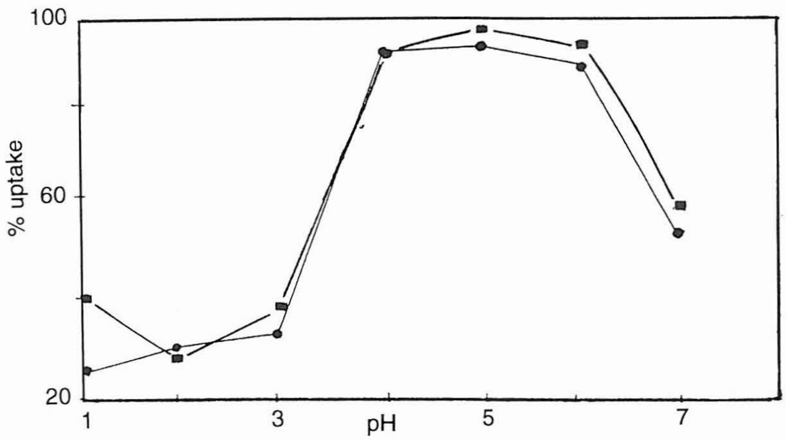

Fig 1. Percentage uptake of Cr(III) as a function of pH.
Substrate: 0.40g rice straw • 0.40g coconut husk ■
[Cr(III) = 20 μg/ml in 50 ml solution]

to desorb 60% and 70% of 19 μg/ml Cr(III) (originally sorbed) by 0.50 g of rice straw and coconut husk respectively. Complete (or 100%) desorption was achieved only by boiling, indicating strong residual binding force between Cr(III) ion and the substrate.

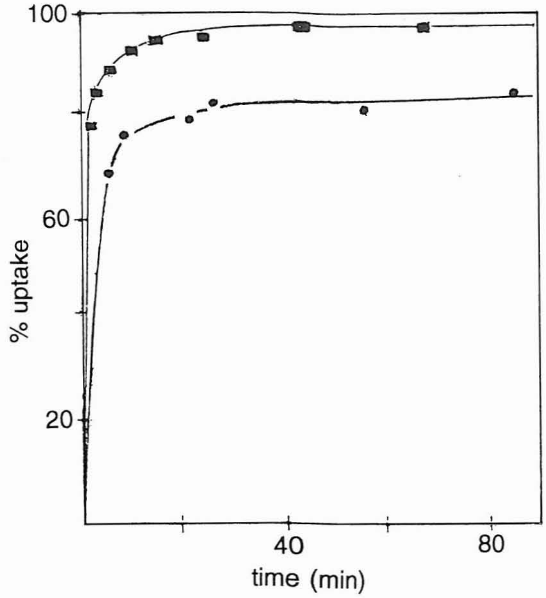

Fig. 2. Percentage uptake of Cr(III) as a function of time 2.0g rice straw • 2.0g coconut husk ■ [Cr(III)] = 25 mg/ml in 800 ml solution]

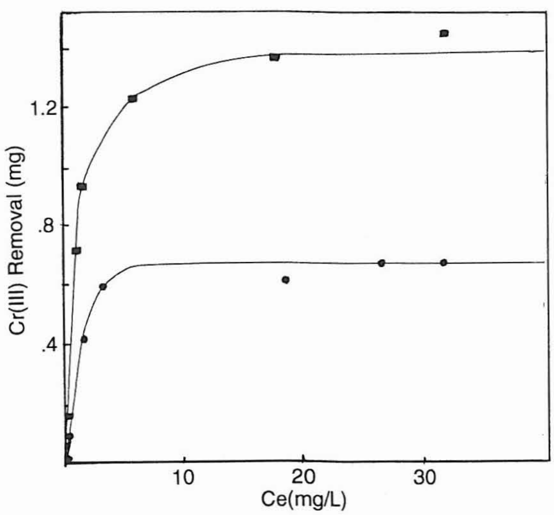

Fig. 3. Adsorption isotherm of Cr(III) at pH 4.5 0.05g rice straw • 0.05g coconut husk ■

Effect of Varying Initial Metal Ion Concentration

The data in *Fig. 2* show that the metal ion uptake by coconut husk and rice straw is concentration-dependent. The sorption capacity was estimated to be 0.55 and 0.30 millimole Cr(III) ion/g substrate for coconut husk and rice straw respectively.

Sorption Kinetics

The data in *Fig.3* show that the sorption equilibrium between 25 μg/ml Cr(III) and 2.0 gm coconut husk or 2.0 gm rice straw is established within 30 minutes. The plot of log C vs t (not shown) produced a linear graph indicating a first order rate reaction.

Column Studies

The data in *Fig. 4* show the breakthrough curves for mixed media column of RS/soil/sand. The top layer (a) was 1.7 cm and the bottom layer (b)

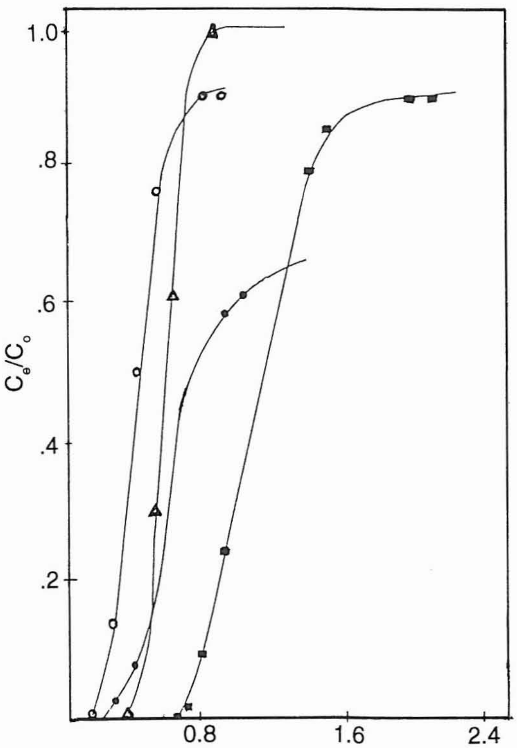

Fig. 4. Breakthrough curves of rice straw/soil/sand columns
rice straw (1.7 cm) + soil (10.3 cm) ■ *soil (1.7 cm) + sand (10.3 cm) o*
rice straw (1.7 cm) + sand (10.3 cm) Δ sand (1.7 cm) + soil (10.3 cm) •
C_o = initial concentration of Cr(III) = 50 μg/ml C_e = effluent concentration of Cr(III)

10.3 cm in height. The low flow rate of 2 ml/min was used as it simulated environmental flow conditions. When 50 μg/ml Cr(III) ion solution was used, the 50% breakthrough point for (sand (a) + soil (b)) column occurred at the passage of 800 ml of solution. This is smaller than the corresponding curves of (RS(a) + soil (b)) column where 50% breakthrough point occurred at 1254 ml. It indicates the presence of significant amounts of binding sites for metal ions in rice straw. The high purity quartz sand used contains no organic matter and hence no binding sites are available.

Using sand as a control, the 50% breakthrough for (sand + soil) and (RS + sand) columns should be equivalent to the 50% breakthrough point for (RS + soil) column. Experimentally, the (RS + soil) column showed a 50% breakthrough point at a passage of 1254 ml of 50 μg/ml Cr(III) ion solution which is quite close to the calculated value of 1440 ml. The 15% discrepancy from the actual value can be attributed to experimental error.

It appears that the addition of substrate such as rice straw to the environment, such as in landfills, would enhance the immobilization of metal ions as demonstrated above. The thicker the layer of rice straw used the greater the enhancement effect in the immobilization of metal ions. A similar trend was observed when coconut husk was used.

ACKNOWLEDGEMENTS

The authors wish to thank Universiti Pertanian Malaysia for providing research funds and Puan Noraini bt. Hj. Abu Bakar for the typing of the manuscript.

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