

## Removal of Linear Alkyl Benzenesulphonate by Quaternized Rice Husk

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### ABSTRACT

Potensi menggunakan serbuk padi terubahsuai sebagai bahan penyerap untuk memisahkan alkil benzenesulfonat linear dari larutan akueus dikaji selidik. Kedua-dua kajian kelompok dan kolum dikajikan. Dari keputusan kajian kelompok, didapati jerapan adalah dipengaruhi oleh faktor pH, dengan jerapan maksimum diperolehi pada pH 2.2. Pemisahan alkil linear meningkat bila suhu meningkat dari 4 kepada 50°C; dan selepas itu pemisahan kekal pada kadar malar dengan peningkatan suhu yang berterusan. Kehadiran anion-anion seperti  $\text{Cl}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  dan  $\text{SO}_4^{2-}$  sedikit mempengaruhi jerapan. Data eksperimen boleh memenuhi isoterma Langmuir dengan kapasiti jerapan maksimum 243.9 mg/g pada pH 2.2 dan  $28 \pm 2^\circ\text{C}$ . Dalam kajian kolum, keputusan menunjukkan bahawa terdapat hubungan linear di antara masa layangan dan ketinggian kolum tetapi kadar aliran influen tidak mempengaruhi masa pemunculan bila kadar lebih daripada 10ml/min.

### ABSTRACT

The potential for the use of quaternized rice husk as a sorbent for the removal of linear alkyl benzenesulphonate from aqueous solution was investigated. Both batch and column studies were carried out. The results of the batch studies indicate that sorption was pH dependent, with maximum sorption being attained at pH 2.2. The removal of linear alkyl increased as the temperature increased from 4 to 50 °C; thereafter uptake remained constant with further increase in temperature. The presence of anions such as  $\text{Cl}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{SO}_4^{2-}$  had little effect on sorption. Experimental data could be fitted into the Langmuir isotherm with a maximum sorption capacity of 243.9 mg/g at pH 2.2 and  $28 \pm 2^\circ\text{C}$ . In the column studies, results show that a linear relationship existed between service time and bed-depth. However, flow rate of influent had no effect on breakthrough time once it was above 10 ml/min.

**Keywords:** linear alkyl benzenesulphonate, sorption, isotherm, quaternized rice husk

### INTRODUCTION

Surfactants are the principal active ingredients in detergents and cleansing agents, in both industrial and domestic applications. Alkyl benzenesulphonates (ABS) have been the most important anionic surfactants since the early 1960s because of their low production cost and good cleaning ability (Cannon 1973). The resistance of branched-chain alkyl benzenesulphonates to bacterial

degradation has led to their replacement by the linear compounds for the last 20 years. Although linear alkyl benzenesulphonates (LAS) are more rapidly biodegradable, they still have adverse environmental consequences and pose a threat to aquatic life forms. Research has shown that concentrations as low as 5 g/l could impair the metabolic process of fish fingerlings (Misra *et al.* 1991). The biodegradation of commercial LAS was found to yield nondegraded metabolites which consisted of benzene moieties (Kolbener *et al.* 1995). In addition, surfactants are able to form stable foam in water at concentrations as low as 1 mg/l (Swarup *et al.* 1992). Hence conventional wastewater treatment may not be sufficient and additional processes are required for the removal of LAS.

Activated carbon and synthetic anion exchange resins have been shown to be effective in the removal of LAS from aqueous solutions (Hinrichs and Snoeyink 1976; Adachi *et al.* 1990). However, the cost of these treatments is relatively high. In recent years there has been tremendous efforts to search for low-cost materials as sorbents for the removal of organic and inorganic pollutants from aqueous systems. The materials investigated include sawdust (Srivastava *et al.* 1986), rice hulls (Nawar and Doma 1989), chitosan (Saucedo *et al.* 1992), chrome sludge (Lee *et al.* 1996), sugar cane bagasse (Laszlo 1996), spent bleaching earth (Lee *et al.* 1997) and modified rice husk (Low and Lee 1997). Fernandez *et al.* (1995, 1996a) reported that algal residues from the extraction of agar-agar could be used as a biosorbent to remove LAS and the maximum sorption capacity appeared to be comparable to that reported in the removal of the branched compound by activated carbon. In a study on the use of seed pods from *Albizia lebbek* for the removal of LAS, it was shown that although the maximum sorption capacity of seed pods was lower than that of algal residues, the rate of sorption was more rapid, hence rendering the seed pods a more appropriate biosorbent material at initial concentrations lower than 58 mg/l (Fernandez *et al.* 1996b).

Rice husk, an agricultural byproduct, contains cellulose, hemicellulose, lignin and silica (Luh 1980). The high silica content (ca. 20%) gives it the structural strength as a sorbent without having to go through a cross-linking process. Earlier studies have shown that it is a good sorbent for a variety of metal cations and cationic dyes (Marshall *et al.* 1993; Suemitsu *et al.* 1986). When rice husks were modified through quaternization, they became effective in removing Cr(VI) and reactive dyes from aqueous solutions (Low and Lee 1997; Low *et al.* 1997). In both systems, the positive charge on the quaternized rice husks appeared to play an essential role in the binding of the anionic sorbate. It thus appears that quaternized rice husks may be a suitable sorbent for the removal of anionic surfactants. Hence the investigation on the potential of quaternized rice husks as a sorbent for LAS was carried out and the results are reported here.

## MATERIALS AND METHODS

### *Sorbent Preparation*

Rice husk, obtained from a rice mill, was ground to pass through a 1-mm sieve. Ground rice husk (150 g) was treated with 2 l of 1% w/v  $\text{Na}_2\text{CO}_3$  for 45 min

at room temperature. It was subsequently rinsed several times with distilled water and dried in an oven at 60 - 70°C. The resulting husk was labelled natural rice husk (NRH). A portion of NRH was quaternized according to the method reported by Laszlo (1996) with some modifications. NRH (100 g) was treated with 125 ml of 5 M NaOH for 30 min at room temperature. At the end of the incubation period, 100 ml of 4 M N-(3-chloro-2-hydroxypropyl)-trimethylammonium chloride was added to the mixture. It was thoroughly mixed and left in the oven at 60 - 70°C for 4 h with intermittent stirring. The reaction mixture was then rinsed several times with distilled water and suspended in dilute HCl at pH 2. It was subsequently rinsed with distilled water and dried. The dried product was labelled quaternized rice husk (QRH).

#### *Surfactant Preparation and Determination*

LAS used in this study was the sodium salt of dodecylbenzenesulphonate (BDH, 80%). It was used without further purification. A stock solution of 100 g/l was prepared by dissolving the salt in distilled water. It was subsequently diluted to various concentrations as required by the experiments. The concentration of dodecylbenzenesulphonate (DBS) was determined using a Shimadzu 160 double beam UV spectrophotometer with a 1.0-cm quartz cell at 223 nm wavelength against a distilled water blank.

#### *Batch Studies*

All the experiments were carried out in duplicate. Sorption was measured by equilibrating 0.1 g of QRH/ NRH with 20 ml of 1000 mg/l DBS solution at an agitation rate of 150 rpm for 4 h at room temperature ( $28 \pm 2^\circ\text{C}$ ) unless otherwise stated. A control to ensure sorption of DBS was by QRH or NRH, and not on the surface of the container was included. In addition, a second control to correct for the leachate from QRH at pH 2.2 was established for every test carried out. At the end of equilibration, the reaction mixture was filtered through Whatman no. 1 filter paper before spectrophotometric analysis.

The effect of pH on DBS uptake was studied by equilibrating the reaction mixture at different initial pH values adjusted by the addition of HCl or NaOH solution. To study the effect of contact time and different initial concentrations, DBS solutions of 1000, 1500 and 2000 mg/l were used. At predetermined time intervals, a set of reaction mixture was taken out and analysed. To establish the sorption isotherm, DBS solutions of initial concentrations in the range of 1000 to 3000 mg/l were used. A thermostatic shaking water bath was used to examine the effect of temperature on the sorption of DBS. The experiments were carried out at 4 - 80°C.

An experiment on the effect of other anions on the uptake of DBS on QRH was conducted using solutions containing the surfactant and other anions in concentration ratios of 1:0, 1:1, 1:2, 1:3, 1:4 and 1:10. The anions investigated were chloride, sulphate, hydrogen phosphate and dihydrogen phosphate.

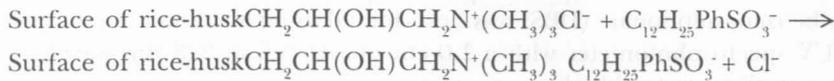
*Column Studies*

Column experiments were conducted using a glass column of internal diameter 1.3 cm. The column was packed to heights of 4.0, 8.0 and 11.4 cm using 0.75, 1.50 and 2.00 g of QRH respectively. DBS solution of concentration 250 mg/l was passed through the column, with the flow rate being varied from 5 to 15 ml/min. The eluant was collected in 25-ml fractions for the 4.0-cm column and 50-ml fractions for the other two columns and analysed for DBS.

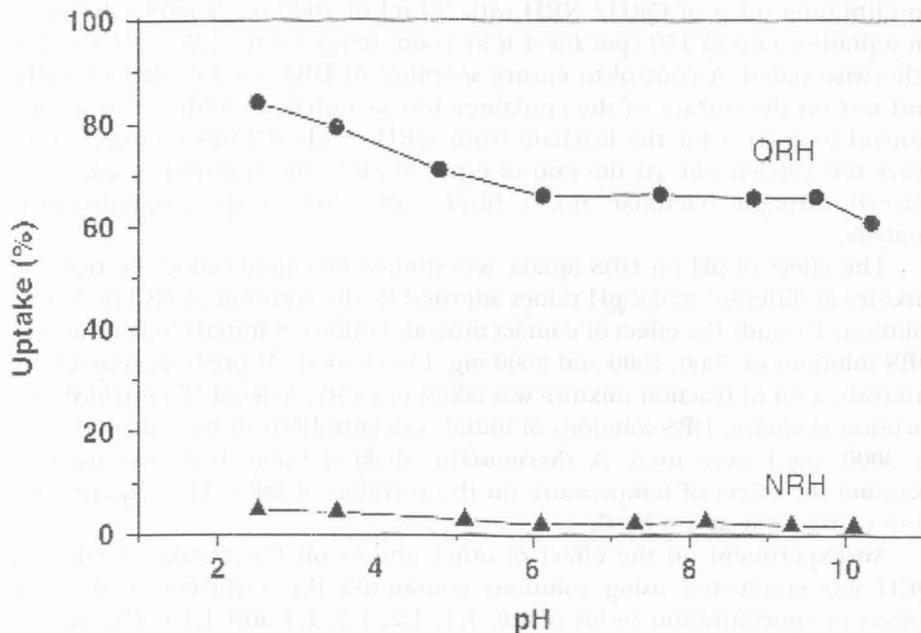
**RESULTS AND DISCUSSION**

*Effect of pH*

The effect of pH on the uptake of DBS by NR and QRH is shown in *Fig. 1*. In the pH range of 2 - 10, QRH exhibited much higher capability to sorb DBS than NR. Sorption of DBS on QRH may be considered an ion exchange process between the dodecylbenzenesulphonate anion and the chloride group of the quaternary amine.



Sorption was highest at pH 2.2 and decreased somewhat with increasing pH; the high sorption capacity of QRH (60%) over a wide pH range (2-10) means



*Fig. 1. Effect of pH on the uptake of DBS by NRH and QRH*

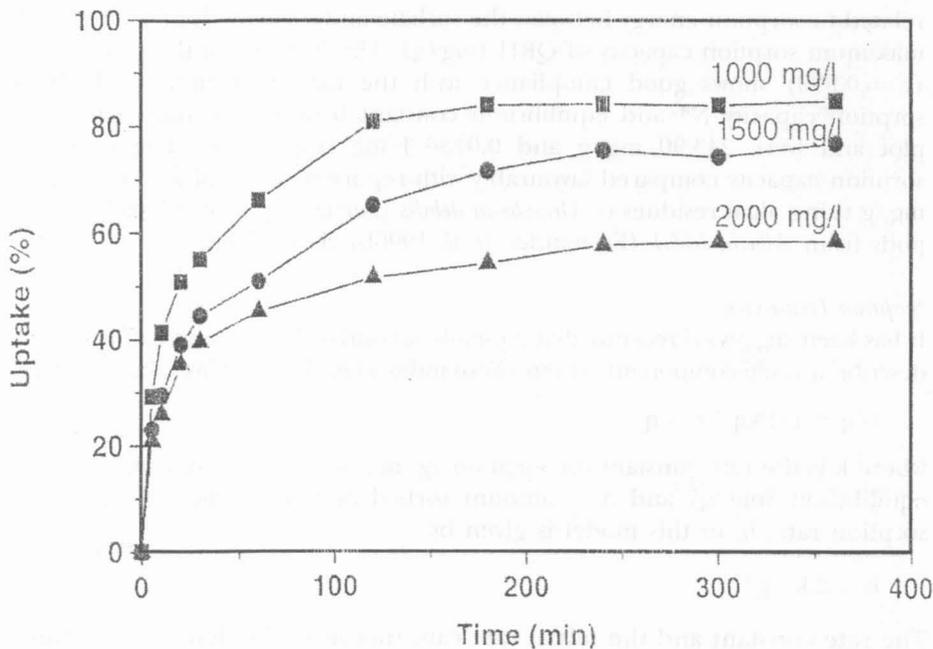


Fig. 2. Effect of contact time and initial concentration on the uptake of DBS by QRH

that QRH could be effective in removing DBS under normal circumstances of effluent discharge. In the present study, in order to explore the maximum capability of QRH in the removal of DBS, subsequent experiments were carried out with solution pH adjusted to 2.2.

#### Effect of contact time and initial concentration

Fig. 2 shows the results of contact time experiments using DBS solutions with initial concentrations of 1000, 1500 and 2000 mg/l. The percent uptake defined as  $[100(C_0 - C_t)/C_0]$  where  $C_0$  is the initial concentration and  $C_t$  the concentration at time  $t$ , follows the usual trend of a greater percentage uptake with decreasing concentration. The initial rate was rapid, irrespective of initial DBS concentration; this was followed by a more gradual process until equilibrium was presumably attained at 240 minutes. This implies that sorption mechanism is complex and probably involves more than one process.

#### Sorption Isotherm

The sorption data for the DBS-QRH system at equilibrium were fitted into a modified Langmuir equation:

$$C_e/N_c = 1/N^*b + C_e/N^* \quad (1)$$

where  $C_e$  is the concentration of DBS solution at equilibrium (mg/l),  $N_c$  the amount of QRH sorbed at equilibrium (mg/g),  $b$  the equilibrium constant

related to sorption energy between the sorbate and sorbent (1/mg) and  $N^*$  the maximum sorption capacity of QRH (mg/g). The linearity of the plot in Fig. 3 ( $r = 0.999$ ) shows good compliance with the Langmuir model. Maximum sorption capacity  $N^*$  and equilibrium constant  $b$  were determined from the plot and were 243.90 mg/g and 0.0186 1/mg respectively. The maximum sorption capacity compared favourably with reported values of 76.34 and 25.43 mg/g using algal residues of *Gracilaria debilis* (Fernandez *et al.* 1996a) and seed pods from *Albizia lebbek* (Fernandez *et al.* 1996b) respectively.

*Sorption Dynamics*

It has been suggested recently that a pseudo second-order reaction can be used to describe a multi-component system (Fernandez *et al.* 1995). This takes the form

$$t/q_t = 1/2kq_c^2 + t/q_c \tag{2}$$

where  $k$  is the rate constant for sorption (g/mg min),  $q_c$  the amount sorbed at equilibrium (mg/g) and  $q_{t_{the}}$  amount sorbed at time  $t$  (mg/g). The initial sorption rate,  $h$ , in this model is given by

$$h = 2.k. q_c^2 \tag{3}$$

The rate constant and the initial rate can, therefore, be determined from a plot of  $t/q_t$  against  $t$ . The sorption data of DBS on QRH were plotted accordingly (Fig. 4) and the regression analysis of the data is given in Table 1. Besides good correlation values ( $r \geq 0.993$ ),  $q_c$  values obtained from the

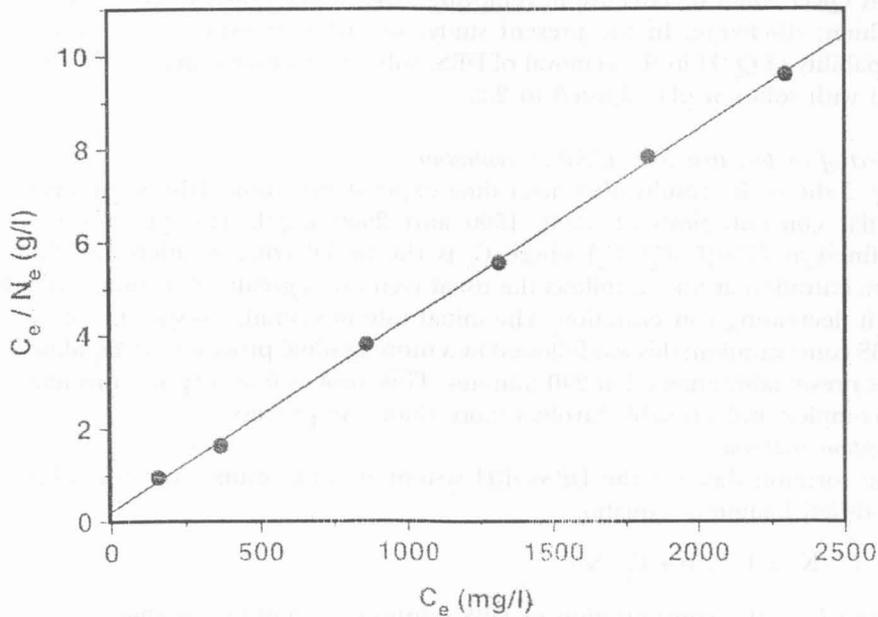


Fig. 3. Langmuir isotherm for the sorption of DBS on QRH

TABLE 1  
Regression data of the pseudo second order rate equation

Initial concentration (mg/l)	Initial rate, h (mg/g.min)	Rate constant, k (g/mg.min)	Uptake at equilibrium, $q_e$ (mg/g)	Correlation coefficient, r
1000	12.58	$2.0 \times 10^{-4}$	175.8	0.996
1500	13.42	$1.5 \times 10^{-4}$	214.1	0.993
2000	19.86	$2.0 \times 10^{-4}$	222.7	0.999

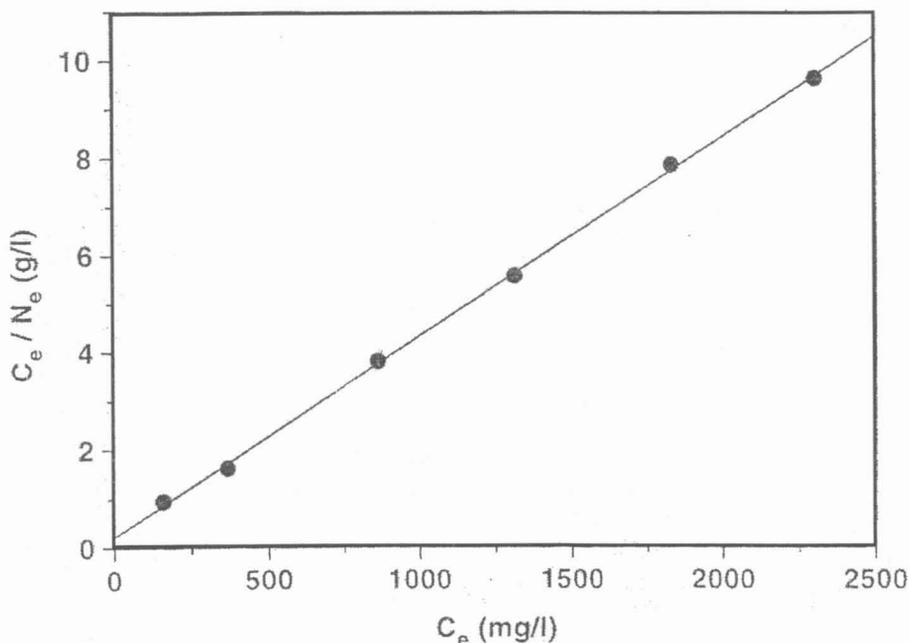


Fig. 4. Plots based on pseudo second order rate equations for QRH at different initial concentrations

plot agreed well with those obtained from time course studies. It thus appears that such a model could describe the kinetics of the sorption process.

#### Effect of Temperature

The variation of uptake with temperature is shown in Fig. 5. As temperature increased from 4 to 50°C, the percentage of uptake increased. Further increase in temperature, however, did not result in any increase in uptake. An increase in temperature would lead to an increase in the mobility of the DBS molecules and hence higher uptake; however a dynamic equilibrium could be attained at temperatures  $\geq 50^\circ\text{C}$ .

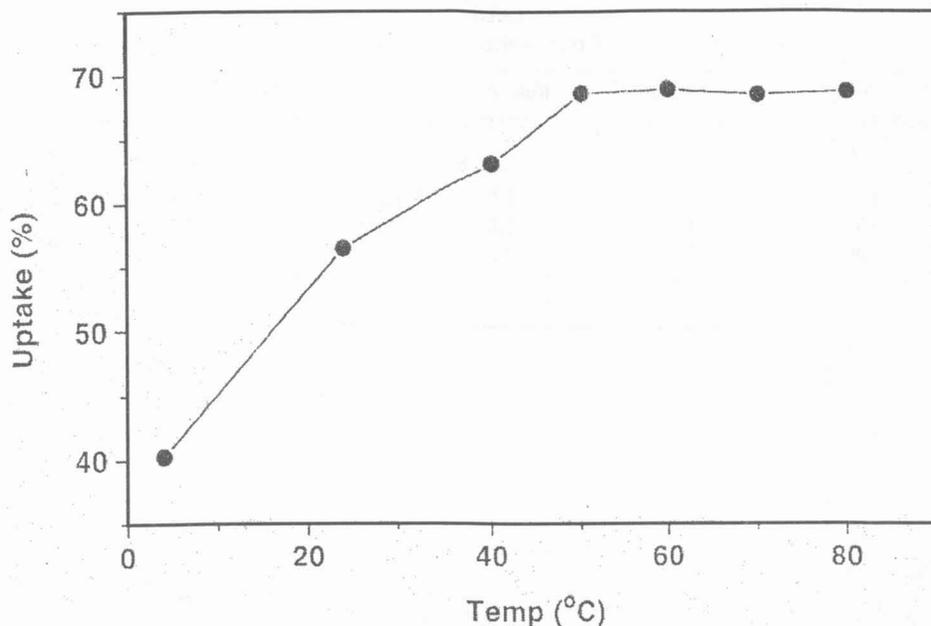


Fig. 5. Effect of temperature on the uptake of DBS by QRH

The relationship between the distribution coefficient,  $K_d$ , defined as  $q_e/C_e$  where  $q_e$  is the amount of DBS sorbed at equilibrium concentration  $C_e$  and the absolute temperature  $T(K)$  of DBS sorption is given by the van't Hoff equation:

$$\text{Log } K_d = \Delta S^\circ / 2.303R - \Delta H^\circ / 2.303RT \quad (4)$$

Such a plot for the DBS-QRH system at temperatures  $\leq 50^\circ\text{C}$  is shown in Fig. 6. The endothermic nature of the sorption process is demonstrated and the enthalpy ( $H^\circ$ ) obtained from the slope of the plot is  $+18.61 \text{ kJ/mol}$ . The results suggest that sorption of DBS on QRH is rather complex and not a simple ion exchange process as the enthalpy associated with ion exchange process is usually smaller than  $8.4 \text{ kJ/mol}$  (Helfferich 1962).

#### Effect of Anions

The effect of other anions on the uptake of DBS under equilibrium conditions is shown in Fig. 7. The presence of  $\text{SO}_4^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{Cl}^-$  does not appear to affect the sorption of DBS on QRH. A previous study on the removal of reactive dyes by quaternized cellulosic material has also shown that the uptake was unaffected by the presence of salts of multivalent anions (Low and Lee 1997). Thus it appears that QRH could be useful in the removal of DBS from effluents that normally contain a mixture of other anions.

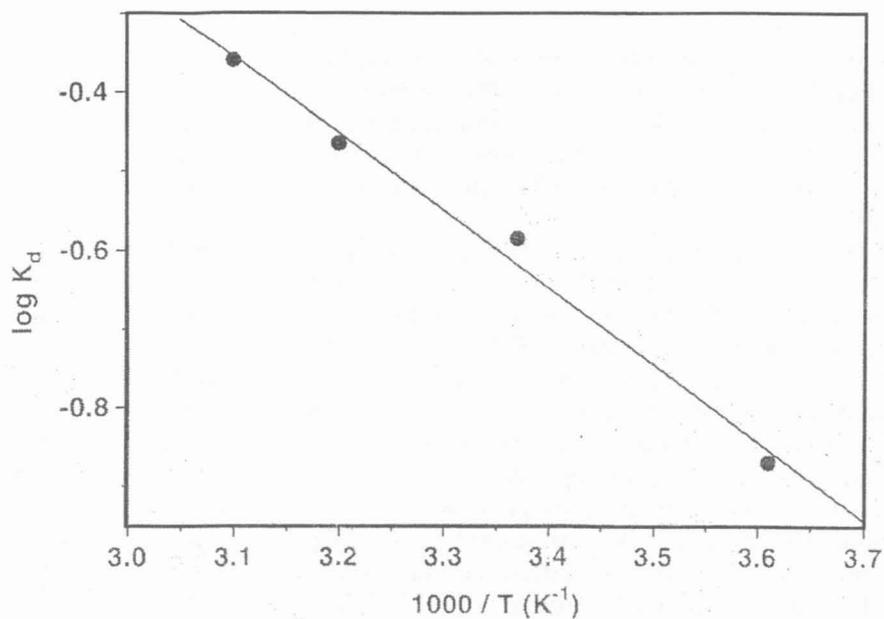


Fig. 6. van Hoff's plot for the DBS - QRH system

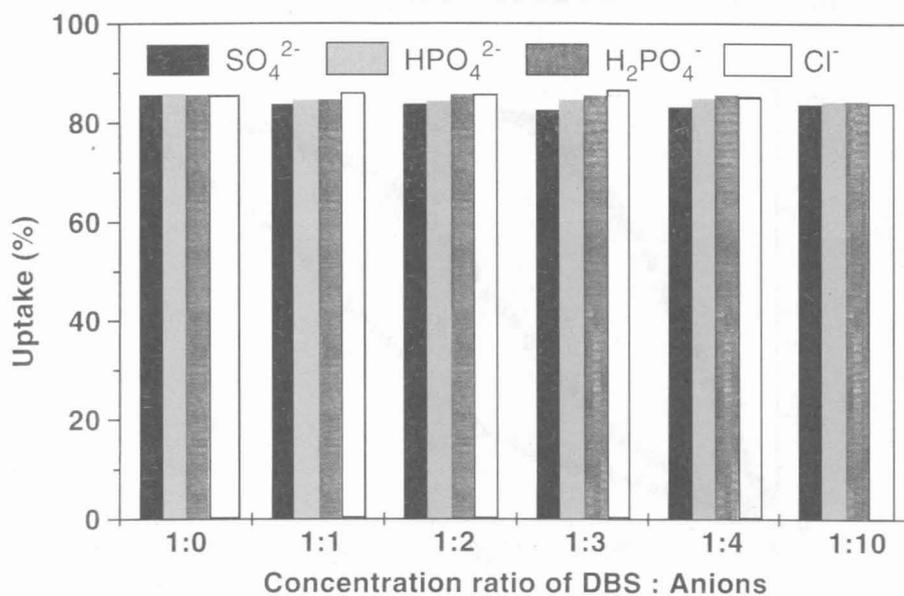


Fig. 7. Effect of anions on the sorption of DBS by QRH

*Column Studies*

Parameters obtained in batch processes are useful in providing information on the effectiveness of the DBS - QRH system. However, the data obtained are generally not applicable to treatment under continuous-flow conditions where the contact time is too short for the attainment of equilibrium. Hence it is necessary to assess the performance of the system under flow conditions.

The breakthrough curves of DBS at a fixed flow rate of 10 ml/min for different bed depths are shown in Fig. 8. It is clear that the higher the bed depth the longer the service time at various breakthroughs. The effect of flow rate on breakthrough is shown in Fig. 9 for a bed depth of 8 cm. At a flow rate of 5 ml/min, 1450 ml of DBS solution could pass through before 50% breakthrough occurred; at 10 and 15 ml/min, the breakthrough volume decreased to 1150 ml and the difference in flow rate did not contribute to any difference in the breakthrough volume. This is due to the rapid sorption process that took place, as has been shown in the batch experiments.

Several models have been proposed to correlate the service time of fixed sorption bed with other operation variables. The bed -depth service time (BDST) model proposed by Hutchins (1973) states that bed depth (H) and service time (t) bear a linear relationship which can be expressed as

$$t = (N_0/C_0 v)H - (v/kN_0)\ln(C_0/C - 1) \tag{5}$$

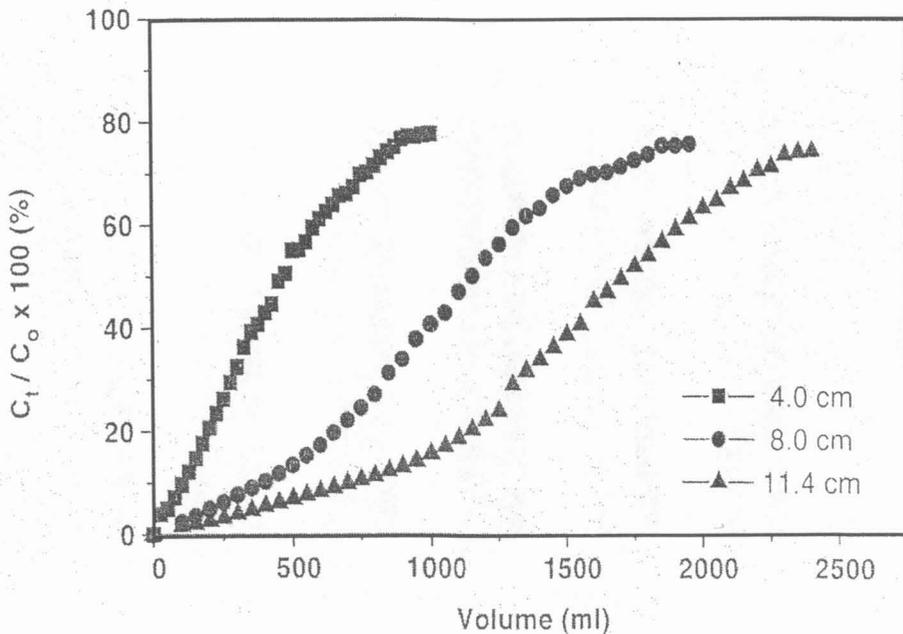


Fig. 8. Breakthrough curves of DBS at various bed depths

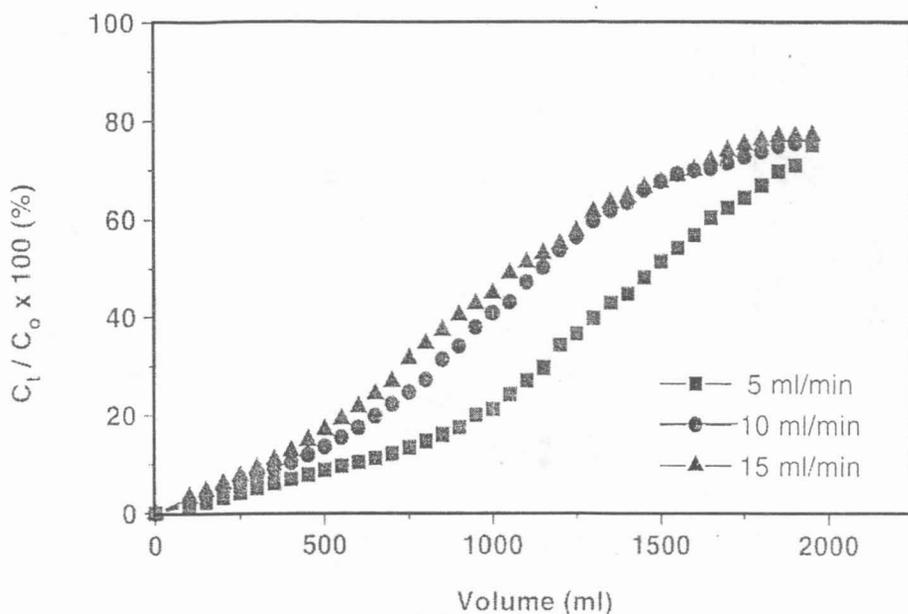


Fig. 9. Breakthrough curves of DBS at various flow rates

where  $t$  is the service time,  $N_0$  the sorption capacity,  $C_0$  the initial concentration, the linear flow rate,  $H$  the bed depth,  $k$  the rate constant of sorption and  $C$  the eluant concentration. At 50% breakthrough ( $C_0/C = 2$ ), the second term in the BDST equation becomes zero giving a simplified equation:

$$t_{0.5} = (N_0/C_0)H \quad (6)$$

Fig. 10 shows the BDST plots at 50% breakthrough at different flow rates (solid lines) for the DBS-QRH system. A linear relationship is obtained, but the lines do not pass through the origin. This deviation is similar to that reported in the adsorption of chromium(VI) using sphagnum-moss peat (Sharma and Forster 1995) when it was suggested the deviation was caused by more than one rate limiting step in the sorption process. The establishment of the BDST equation at a fixed flow rate allows for the calculation of equations at other flow rates. Using the equation for the flow rate of 10 ml/min,  $t_{0.5} = 16.77H - 20.48$ , equations for flow rates of 5 and 15 ml/min were calculated and plotted as dotted lines in Fig. 10. The variation between experimental and calculated values was within 10%.

## CONCLUSION

The present study shows that quaternized rice husk could be used in the removal of linear alkyl benzenesulphonate (LAS) from aqueous solution. Uptake was efficient over a wide range of pH, and maximum sorption capacity based on Langmuir equation compares favourably with previous studies on LAS

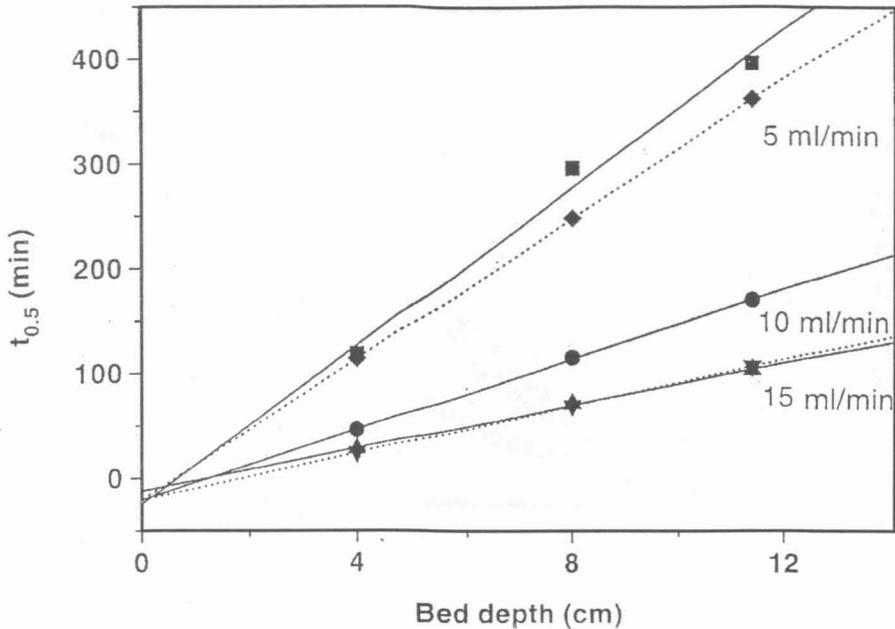


Fig. 10. BDST plots of DBS-QRH system. experimental equations; calculated equations

removal. The rate of uptake was rapid and the presence of other anions, such as phosphates and sulphates, had little interference on uptake. Removal of LAS under continuous flow conditions could be represented by a linear equation relating the service time to bed depth.

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