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Sorption Model of Modified Cellulose as Crude Oil Sorbent

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Abstract: The absorptive behaviour of the three modified cellulose. Cellulose pulps were investigated as crude oil absorbent materials. There three modified cellulose pulps were Benzoyl modified cellulose BMC, Toluenediisocyanate cellulose TDC and toluenediisocyanate cellulose processed by blown TDC^b. the highest adsorption capacities of each of these three modified cellulose pulps were BMC (97.50%), TDC (97.50%) and TDC^b (81.5%) the adsorptive capacities of these modified cellulose pulps for spilled crude oil decrease with increase in quantity of crude oil spilled. The presence of carbonyl functional group in each of these modified cellulose pulps may be responsible for the discrimation of the absorbent between water and crude oil films floating on water surface.

Key words: Crude oil, modified cellulose pulp, sorption model biodegradable, adsorbent

INTRODUCTION

The research into the use of Agricultural by-products and their modified products as absorbents for the removal of crude oil from aqueous solutions have been on the increase. Such biodegradable absorbents of agricultural by-products are straw, rice husks, corncobs, cellulose materials (Schatzerg and Nagy, 1971). These agricultural-by-products and their chemically modified products are naturally occurring, available at little or cost, and biodegradable (Gardea *et al*., 1996; Hazerd, 1999; Gengs, 1998).

The Agricultural-by products and their modified products serve as absorbents for crude oil and its products spill clean up operation in the aqueous environments. These spill are serious environmental pollution.

Pollution is an introduction to any part of the environment substance (s), which has harmful effect on the ecosystem (Rovenberg and Gutrick, 1977).

Crude oil pollution is impairment of the environments with crude oil or its refined products as the major pollutants. These crude oil pollution arise from oil tankers, facture of crude oil pipelines, pipeline vandalization, leaks from bulk cruder oil and its products pollution differ from one environment to another subject to such physical features as land, water surfaces (aqueous environments); sea, estuaries (Ce Ha, 1979). The effects of crude oil and its refined product spills are inhibition of oxidation of marine lives, tumors in fishes, molluses, egg laying and hatching cycle, inhibition of photosynthesis of marine flora (Smith, 1983; Cooney, 1984).

Cellulose and its modified cellulose pulps are used as biodegradable adsorbents in the crude oil and its refined product clean up operations in the aqueous environment. Cellulose is a homopolysaccharide derived from plants.

It is linear compound compose of D-glycopyranose; linked together by 1-4 glycosidic bond (Odu, 1981). Cellulose has a general chemical formula $(C_6H_{10}O_5)$ n where n = 5 or more glucose units. It has three reactive hydroxyl functional groups written as $(C6H_7O_2\ (OH)_3)$ n (1). Cellulose is one of the most abundant polysaccharide in plant kingdom. The natural sources of cellulose are, wood, saw dust, elephant grass, cassava peels waste new sprints, woodbark, corncobs. Cellulose serves as food storage reservoir for plant, plant protective coat, carbohydrates for ruminants, insects, raw materials for paper and pharmaceutical, book binding, printing, packing industries and a host of other uses (Speight, 1981).

This study therefore, reports sorption model and crude oil absorptive behaviour of modified cellulose pulps.

MATERIALS AND METHODS

Sample collection: Crude oil sample was obtained from Port Harcourt crude oil flow station, River state, courtesy of shell petroleum development company Nigeria. Waste

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new sprints were obtained from old new papers dump at Okigwe Imo State, Nigeria. All chemicals used were analytical grade reagents from BDH Chemicals London.

Sample preparation: The collected waste new sprints were shredded into particles of size 250 mm using paper shredder (binatone model). These waste new sprints were used in the preparation of cellulose pulps as described by hunter (American standard for testing and materials, 1993).

The cellulose pulps thus obtained were therefore chemically modified using esterification method (Ewvings, 1985; Willared and Dean, 1974). Forty grams of cellulose pulps was weighed and taken into one litre-volume quick-fixed flask containing dichloromethane solvent (400 mL). Initial refluxing was carried for 30 min at 80°C. Then 80 mL of 10% ethanolic NaOH solution was added as catalyst. Eighty millimeter of benzoylchoride reagent solution was added in a step vise manner during a ten-minutes interval. The whole refluxing exercise was carried for 2.5 h. There after, the solvent used for refluxing was removed by-press-drying the Benzoyl modified cellulose.

The modified product was rendered less hygroscopic by further processing as follows, the product was soaked in a plastic container containing 250 mL and product was stirred repeatedly. The acetone solvent was removed by press drying of the soaked product. The modified product Benzoylmodified cellulose BMC, was spread thin film on a clean wooden slab and air-dried for 24 h.

The procedure described above was used exactly in the manner for carrying out the modification of the other two chemical modification processes. Except that Toluenediisolyanate was used as modifying chemical regents. Again water was used as a blowing agent in the further processing of the Toluenediisocyanate cellulose to form toluenediisocyanate cellulose blown TDC^b.

Adsorption studies: Varying simulated crude oil spills were carried out using 300 mL of natural seawater collected from Onne-sea Port Eleme, Port Harcourt-River state Nigeria.

Five grass vessels were set up each containing 300 mL of natural seawater. Each of these five glass vessels was labeled. Each container (glass vessel) received 0.2, 0.4, 0.8 and 1.0 mL of crude oil, respectively corresponding to 2.0, 3.3, 5, 6.70 and 8.30 mg mL^{-1} of crude oil simulated spills, respectively.

One grams of the benzoyl modified cellulose was uniformly spread over the floating crude oil film in each of the five glass vessels set up. Contact times of 30 min for sorption equilibrium attainment for each of the vessels were monitored.

After each 30 min interval, the floating adsorbent with its content was scooped into a departing flask and the adsorbed crude oil desorbed using 20 mL chloroform, solvent. The crude oil extract from each of the five glass vessels was quantify using spectrophotometric method at 500 nm wavelength (Weiner, 2000). The amount of crude oil sorbed was calculated using direct comparison with standard crude oil sample method (Abia *et al*., 2002). The above experimental procedure was repeated exactly using Toluenediisolyanate Cellulose (TDC) and toluenediisocyanate Cellulose blown (TDC^b) as absorbents respectively.

Equilibrium sorption studies: The Equilibrium sorption was studied by calculating the logarithm of the concentrations amount of crude oil films sorbed and logarithm of the concentration of crude oil spilled using modified freundlich isotherm equilibrium equation

Logct = log Ks + logco …….(18,10) where C_t = amount of crude oil sorbed at constant time (30 min),

Co = initial concentration of crude oil spilled during the simulated spill experiment,

K_d = Partition coefficient of the sorption process.

RESULTS AND DISCUSSION

The data on sorption model and the use of modified pulps as crude oil absorbent for the removal of crude oil file from surface water are presented in this work. The sorption capacities of the three modified cellulose materials: benzoyl modified cellulose BMC, Toluenediisocyanate cellulose TDC and Toluenediisocyanate cellulose blown TDC^b at difference spilled crude oil concentrations are given in Table 1. The results in Table 1 indicated that the sorption of cruder oil by these modified cellulose materials decreases with increase in the initial concentrations of crude oil spilled in the simulated spill experiments.

The effect of concentrations on the sorption capacities of these modified cellulose, material is showed in Fig. 1.

Figure 2 shows a liner trend with peak areas for each of the three modified cellulose materials.

The sorption capacities of the three modified cellulose materials were further examined using modified sorption isotherm model. The model is represented in Eq. 1. The logarithmic values for the initial concentrations of the crude oil spill log C_o, and the amount of corresponding crude oil films sorbed at time t (log C_t) is shown in Table 2.

The constant log K_d, in the modified freundlich isotherm have been determined for each of these, modified

Table 1: Effect of concentrations of crude oil films on absorptive of modified cellulose adsorbents

Initial concentrations of spilled crude oil mg mL^{-1} Co	Amount of crude oil films absorbent at time t, Bmc (mg mL^{-1})	TDC (mg mL^{-1})	TDC^b (mg mL^{-1})
2.00	1.95	1.95	1.63
3.30	2.07	2.04	2.00
5.00	2.30	2.10	2.10
6.70	2.67	2.12	2.18
8.90	2.69	2.14	2.29

Values are mean of four determinations

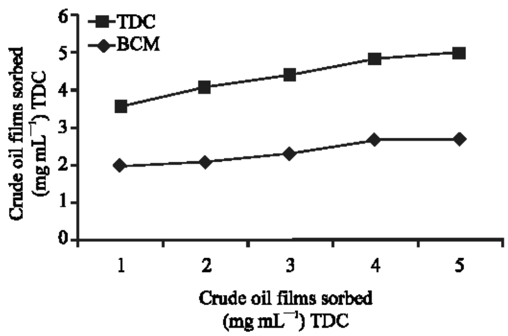

Fig. 1: Amount of crude oil films sorbed (mg mL^{-1})

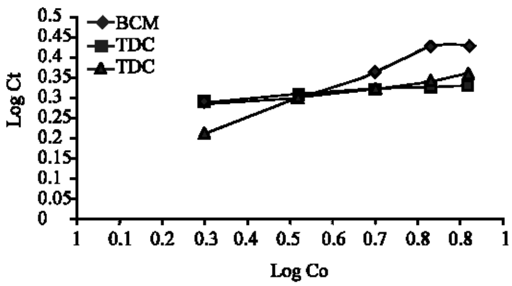

Fig. 2: The values of logarithm of Co and Ct of modified cellulose adsorbents

cellulose materials and are listed in Table 3. The equilibrium constant K_d, for each of these modified cellulose materials could be used as indicator to establish the sorption capacities of the modified cellulose material and also the particles size of absorbents.

From Table 3, the trend in K_d values are TDC> BMC> TDC^b.

In general, the amount of crude oil films sorbed by each of these modified cellulose materials decreases with increase in the initial concentration of crude oil spilled on the surface water. This effect suggests that the sorption mechanism may be absorption process. Again the sorption mechanism is stable, fast process which means that the absorption is taking place inside the pore matrices of the modified cellulose materials created by cross-linking affect of the carbonyl group present in each of these modified cellulose materials.

Table 2: Values of logarithm of initial concentrations (Co) and amount of crude oil absorbed at time t C_t of the modified cellulose absorbent

Log Co	Log Ct	Log Ct TDC	Log TDC^b
0.300	0.290	0.290	0.212
0.520	0.301	0.310	0.300
0.700	0.362	0.322	0.322
0.830	0.427	0.326	0.339
0.920	0.430	0.330	0.360

Table 3: Equilibrium constants for the three modified cellulose absorbents: BMC, TDC and TDC^b

Equilibrium constants	BMC	TDC	TDC^b
K_d	1.84	1.86	1.32

Where K_d = partition coefficient for sorption $K_d = C_t/C_o$ ....(2) [18]

The desorption studies for the recovery of the crude oil sorption from each of these modified cellulose materials BMC, TDC, and TDC^b respectively using chloroform solvent illustrated, the potential of recycling these materials and subsequent reuse in another round of crude oil films clean up operations. Once the crude oil is removed, the modified cellulose material, which is biodegradable, can be disposed off without any environment damage. Hence these modified cellulose materials could be used for cleansing the aquatic environment of spilled crude oil films arising from crude oil exploration, utilization and transportation of refined petroleum products.

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