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Immobilization of urea with oxidized and unoxidized lignocellulosic materials

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Urea fertilizer was immobilized with modified and unmodified lignocellulosic materials. The amounts of urea immobilized at 27·0°C were 14·8, 10·8, 19·7, 20·1, 22·3, 28·3 and 36·6 mg per g of unmodified softwood, hardwood, millet, guinea corn and maize stalks, acha and rice straws, respectively. For lignocellulosic materials modified by periodate oxidization, 27·0, 21·0, 35·2, 39·3, 41·5, 49·1 and 52·7 mg per g of softwood, hardwood, millet, guinea corn and maize stalks, acha and rice straws, respectively, of urea were immobilized. Poor immobilization was observed for unmodified lignocellulosic materials at higher temperatures; whereas maximum immobilization was achieved at higher temperatures for modified lignocellulosic materials up to 50·0°C; beyond this no further immobilization was observed. The incubation time for achieving maximum immobilization was 24 h.

INTRODUCTION

Urea, when applied in tropical countries where rainfall is heavy, is easily leached away. Consequently, urea fertilizer and other very soluble fertilizers have to be applied two or three times before the crop is matured. There is need, therefore, to find a way of slowing down the rapid leaching, consequently reducing cost.

Periodate oxidized or very porous lignocellulosic materials in granular form can be used to immobilize urea by way of hydrogen bonding or some other mechanism, thereby slowing down rapid leaching. Lignocellulosic materials are not expensive, and often they are burnt by farmers resulting in a loss of volatile materials. These materials will also hold moisture, thus keeping the soil moist, and will eventually be degraded by microorganisms into much needed humus.

In addition to providing the nitrogen requirement, urea helps to neutralize soil acidity without the possible negative effects of calcium hydroxide, which when wrongly applied leads to excessive soil alkalinity.

This work reports the immobilization of urea on several lignocellulosic materials in modified and unmodified forms using local agricultural waste.

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MATERIALS AND METHODS

Materials

All chemicals used were of standard grade obtained from British Drug Houses Limited (BDH), UK. The sawdusts, millet, guinea corn and maize stalks, acha and rice straws were obtained from Benue and Plateau States of Nigeria.

Milling of the lignocellulosic materials

The sawdusts were collected from the saw mill in milled forms. The millet, guinea corn and maize stalks, acha and rice straws were hammer milled, then ball milled and sieved. Samples in the range, 20, 30–40 and 60–100 mesh sizes were used in this work.

Modification of the lignocellulosic materials

The lignocellulosic materials (10·0 g) were each separately treated with potassium periodate (0·01 M, 100 ml) (Nevell, 1957) for 3 h, filtered through a nylon cloth under vacuum, washed with distilled water (3 × 100 ml) and then dried in the open air for 24 h.

Immobilization of urea fertilizers

Duplicate samples of modified and unmobilized lignocellulosic materials (0·1 g) were added to various concentrations of urea solutions (1·0–15·0 g/litre, 25·0 ml). The mixtures were incubated at 27·0°C and samples (2·0 ml) were withdrawn at intervals and filtered through a nylon cloth under vacuum.

The effect of temperature on the urea uptake

The above procedure was repeated at various temperatures and the urea uptake assayed as below.

Total urea uptake assays

The filtrates obtained from the immobilization experiment (1·0 ml) were hydrolysed with sulphuric acid (96%, 0·50 ml) in a boiling water-bath for 5 min. The resulting solutions were made up to 10·0 ml with sodium acetate buffer (0·2 M, pH 5·5). Aliquots of the diluted samples (1·0 ml) were mixed with 1·5 ml of ninhydrin reagent (ninhydrin, 4·0 g and hydrindantin, 0·88 g in 100 ml of 2-methoxyethanol and 1·0 ml sodium acetate (2 M, pH 5·5) in stoppered test tubes and heated for 10 min in a boiling water-bath. The solutions were diluted immediately without prior cooling (to 10·0 ml) with precooled (0°C) formaldehyde diluent (formaldehyde, 0·5% v/v in isopropanol-water 1:1) and the absorbance at 570 nm was determined using an SP-20 spectrophotometer. A calibration curve was constructed, using ammonium chloride as the standard.

RESULTS AND DISCUSSION

The uptake of urea by lignocellulosic materials for various mesh sizes of all the lignocellulosic materials used increased with smaller particle sizes (Table 1). This shows that for a given weight of sample, an increase in exposed surface area by way of fine particles enhances urea uptake, due to the fact that the contact between urea and lignocellulosic materials is increased. The urea uptake for a given size of lignocellulosic material was observed to be less for more crystalline materials than for the more amorphous materials (Table 1). The uptake in increasing order was hardwood, softwood, then the straws, again in order of their percentage of crystallinity. This is probably due to the fact that it is easier for urea to penetrate the amorphous materials, and therefore have contact with more of the interior than with the more crystalline samples, which are more difficult to penetrate. The above factors have earlier been reported to affect hydrolysis of lignocellulosic materials by acid and enzymic hydrolysis as well as other chemical reactions (King & Vessals, 1969; Sasaki *et al.*, 1979; Buriquez, 1981; Moreria *et al.*, 1981; Ryu *et al.*, 1982; Shambe & Kennedy, 1984, 1985).

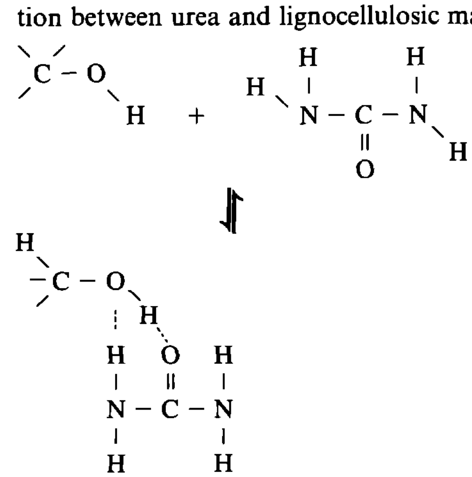
Table 1. Urea immobilization with oxidized and unoxidized lignocellulosic materials of various mesh sizes at 27·0°C

Lignocellulosic materials (LGC)	Amount of urea immobilized ($mg\,g^{-1}$ LGC)		
	20 mesh	30–50 mesh	60–100 mesh
Softwood[a]	1·8	4·6	14·8
Softwood[b]	2·8	10·2	27·0
Hardwood[a]	0·9	3·5	10·8
Hardwood[b]	1·6	8·5	21·0
Millet stalk[a]	3·0	7·2	19·7
Millet stalk[b]	6·0	15·1	35·2
Guinea Corn stalk[a]	3·2	7·8	20·1
Guinea Corn stalk[b]	6·5	17·0	39·3
Maize stalk[a]	3·7	8·3	22·3
Maize stalk[b]	7·0	18·9	41·5
Acha straws[a]	4·1	9·6	28·3
Acha straws[b]	9·1	19·2	49·1
Rice straws[a]	6·1	12·0	36·6
Rice straws[b]	10·2	20·1	52·7

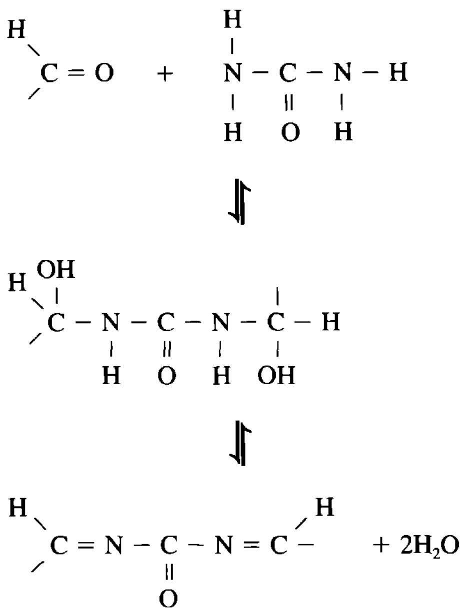
[a]Lignocellulosic materials.
[b]Oxidized lignocellulosic materials.

There was a significant increase in urea uptake as a result of periodate oxidation of lignocellulosic materials for the various particle sizes (Table 1). The increase in urea uptake was higher for the finer particles, probably due to greater availability of surface area for attack by the oxidizing agents, consequently producing more active sites for chemical reactions to take place when urea was in contact with lignocellulosic materials. Similarly, the increase in urea uptake per given particle size was highest for the more amorphous particles, probably because of the ease with which oxidizing agents penetrate lignocellulosic materials, resulting into oxidation of the inner particles and thus creating active sites in the interior. For the highly crystalline sections, this is not possible.

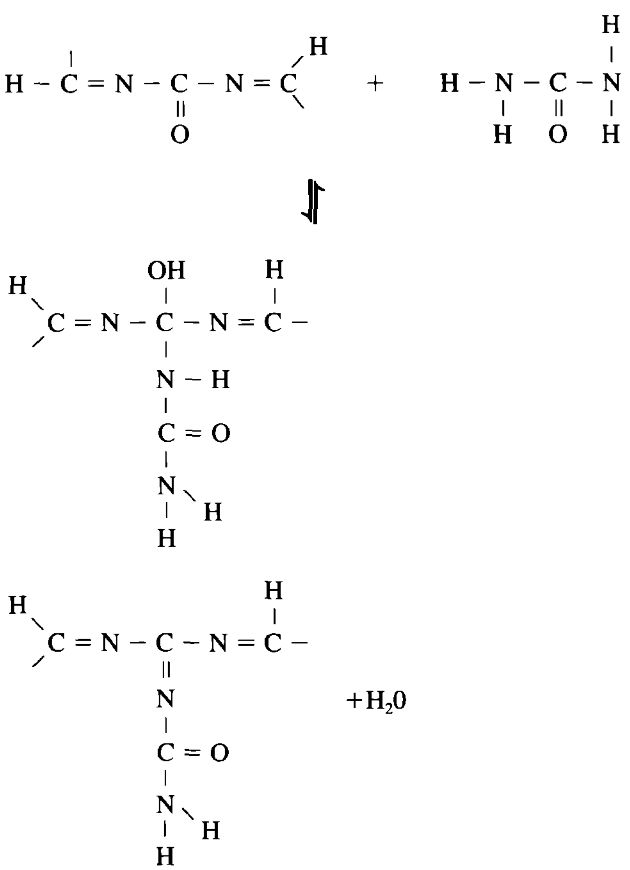
The linkages of polysaccharides in lignocellulosic materials is B-D-(1–4) linkage for hemicelluloses as well as celluloses. Mild periodate oxidation is thus mostly between carbons 2 and 3, producing carbonyl groups on these two carbons. Any group on lignin non-aromatic sections with adjacent hydroxyl groups may be similarly oxidized. The aromatic ring may not be significantly oxidized since the oxidation is mild. The possible reaction between urea and lignocellulosic materials is:



The remaining hydrogens on nitrogen can form hydrogen bonds with other hydroxyl groups on lignocellulosic materials. The carbonyl groups on lignocellulosic materials react in addition to hydrogen bonds as follows:



It is possible for urea to attack the above product.



A temperature increase is also observed to have a significant effect on urea uptake by lignocellulosic materials. The amount of urea uptake increases with temperature up to 50°C (Figs 1 and 2). Values observed for non-oxidized lignocellulosic materials (up to 50°C) were similar to those observed at 27°C (Table 1).

Higher concentrations of urea appear to push the reaction faster to higher urea uptake (Fig. 3), showing that it is highly reversible and an increase in one of the reactants must of necessity result in the increase of the products to maintain equilibrium.

CONCLUSION

It may be stated that the use of lignocellulosic materials in immobilizing nitrogenous fertilizer is an effective way of tackling problems associated with their applications, particularly soil conservation which is currently a major menace to agriculture in the tropics. Indeed the acha

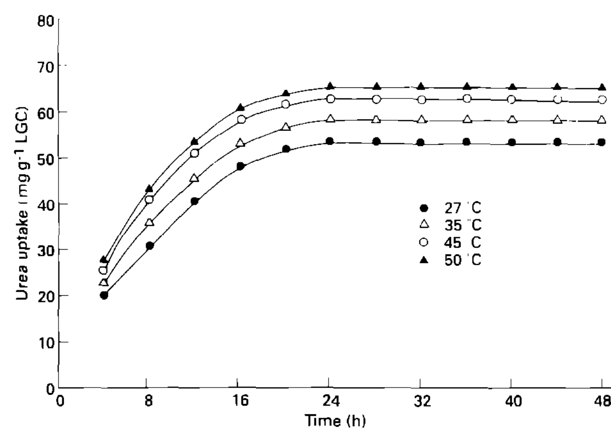


Fig. 1. Plots of uptake versus time for immobilization of urea with pre-treated rice straw (60–100 mesh); condition: $16{\cdot}0 \times 10^{-2}$ M urea concentration.

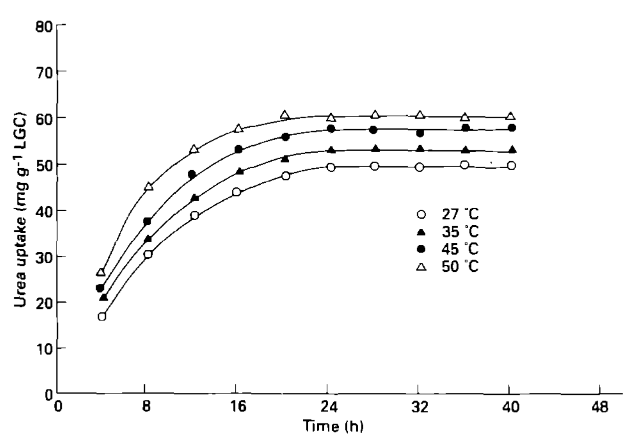


Fig. 2. Plots of uptake versus time for immobilization of urea with pre-treated acha straw (60–100 mesh); condition: $16{\cdot}0 \times 10^{-2}$ M urea concentration.

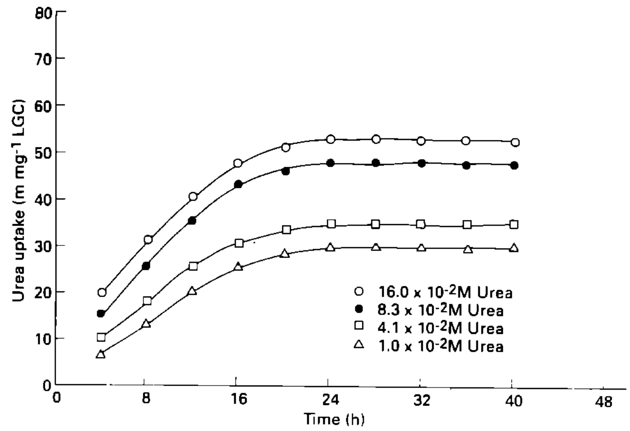


Fig. 3. Plots of uptake versus time for immobilization of urea with pre-treated rice straw (60–100 mesh); condition: 27·0°C.

and rice straws, observed to be the best for immobilization, are abundant and cheap. It is hoped that the methodology promoted in this work will be applicable to the problems of straws and stalks disposal currently encountered all over the world.

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