

PHYSICO-CHEMICAL STUDIES OF THE ADSORPTION OF UREA AND MELAMINE ON SAWDUST

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ABSTRACT

Three different concentrations, 0.5g/100cm³, 1.0g/100cm³ and 1.5g/100cm³ of urea and melamine respectively, were used for the physical modification of saw-dust using batch equilibration method. The results show that there was increased adsorption with time and concentration for the systems considered. However, the results show that the quantity of melamine adsorbed by saw-dust was greater than that of urea under the same conditions. The shapes of the curves for all the adsorption processes studied were similar to the Langmuir Isotherm type (L-curve) depicting a monolayer adsorption. Also the uptake of melamine and urea by saw-dust was found to be affected positively by temperature. This increase in adsorption with increase in temperature was encouraged by the swelling phenomenon associated with saw-dust. This observation is evident from the adsorptive capacities of the adsorbent at various temperatures. The mechanism of adsorption could not be completely defined but is believed to be mediated through physical (van der waals) as well as hydrogen bonding.

INTRODUCTION

The adsorption of bioactive substances on polymers has been investigated by various researchers especially in the areas of pharmacy and medicine. The adsorption of chlorpromazine hydrochloride by wool, erythrocytes by tissues was reported by Besson et al¹. Saleh and Nasipuri² studied the adsorption of benzoic acid on sulphadimidine. Porubcan et al.³ studied the mechanism of adsorption of chindamycin and tetracycline by montmorillonite, and the adsorption of certified dyes by starch has been investigated by Zograf and Mattocks⁴. The adsorption of medicinally active compounds by various types of adsorbents has been reported by other investigators⁵⁻¹⁰. In all these investigations, the adsorption isotherms of the various systems have been studied. The classical approach indicates the quantity of compound adsorbed, the rate and other physical parameters.

In all the above, however, not much work has been done on the adsorption of bioactive

substances on polymers with emphasis on agricultural application as it relates to fertilizer. Several workers have worked on bioactive substance/polymer combinations, with those researches being solely based on the chemical modification of polymers to obtain slow release or sustained release system without due attention to the physical modification of these polymers with their attendant properties.

The purpose of this work was to investigate the adsorption of such high nitrogen containing bioactive compounds as urea and melamine which possess one of the necessary nutrients for plant growth on such biodegradable natural polymers as saw dust, and to determine the effect of concentration and temperature on the adsorption.

It was felt that studies concerned with plant nutrient affinity for biodegradable polymer substrate would be of value to those concerned with this problem especially in third world countries where inorganic fertilizers are repeatedly applied to the soil. It is envisaged

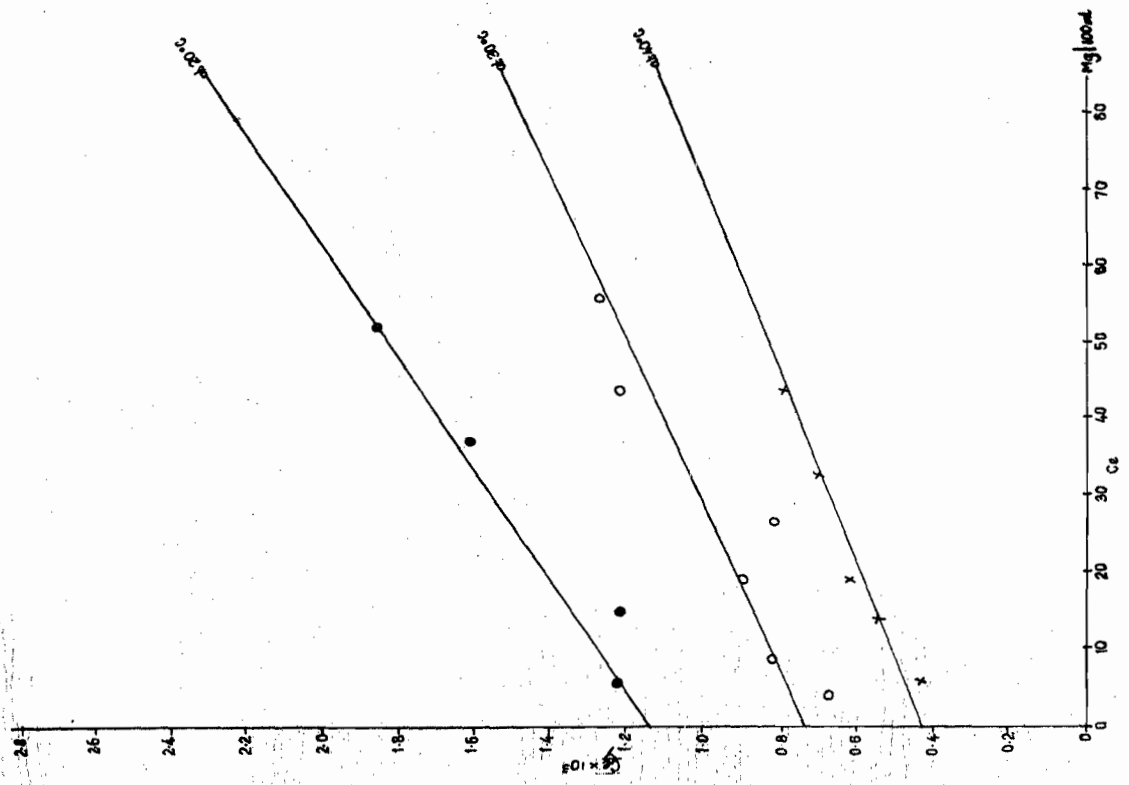


Fig 4: Langmuir's plot of $C_e \times 10^3$ vs Equilibrium concentration C_e of Melamine on lg saw-dust at various temperatures.

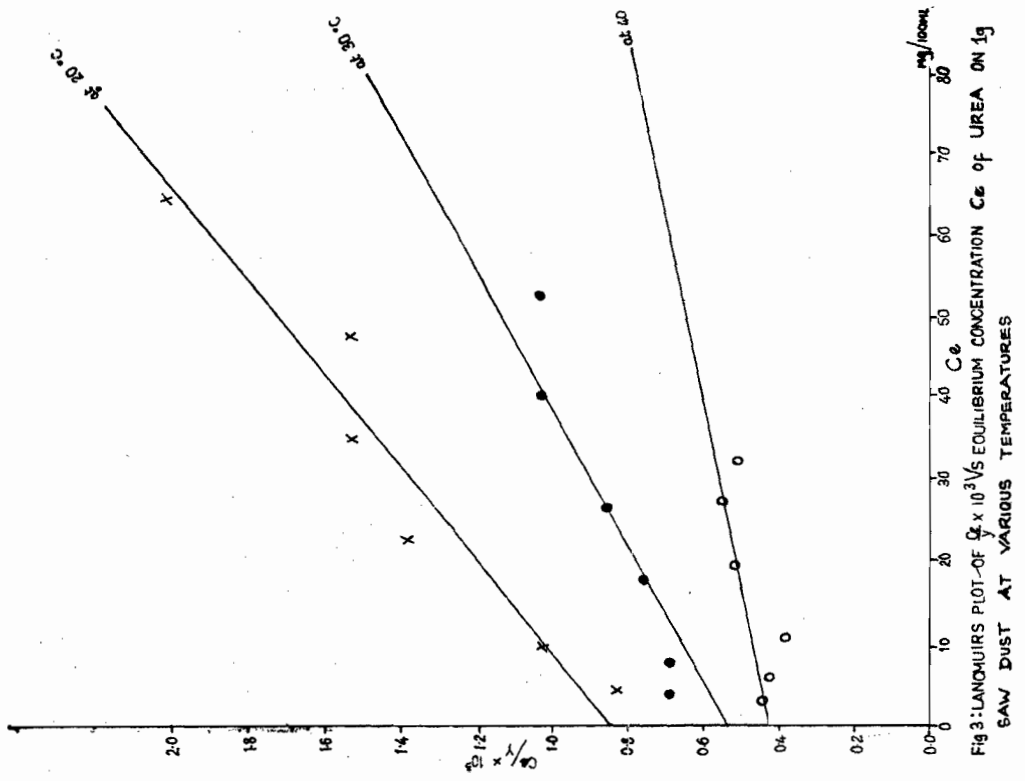


Fig 3: LANGMUIR'S PLOT OF $C_e \times 10^3$ VS EQUILIBRIUM CONCENTRATION C_e OF UREA ON LG SAW DUST AT VARIOUS TEMPERATURES

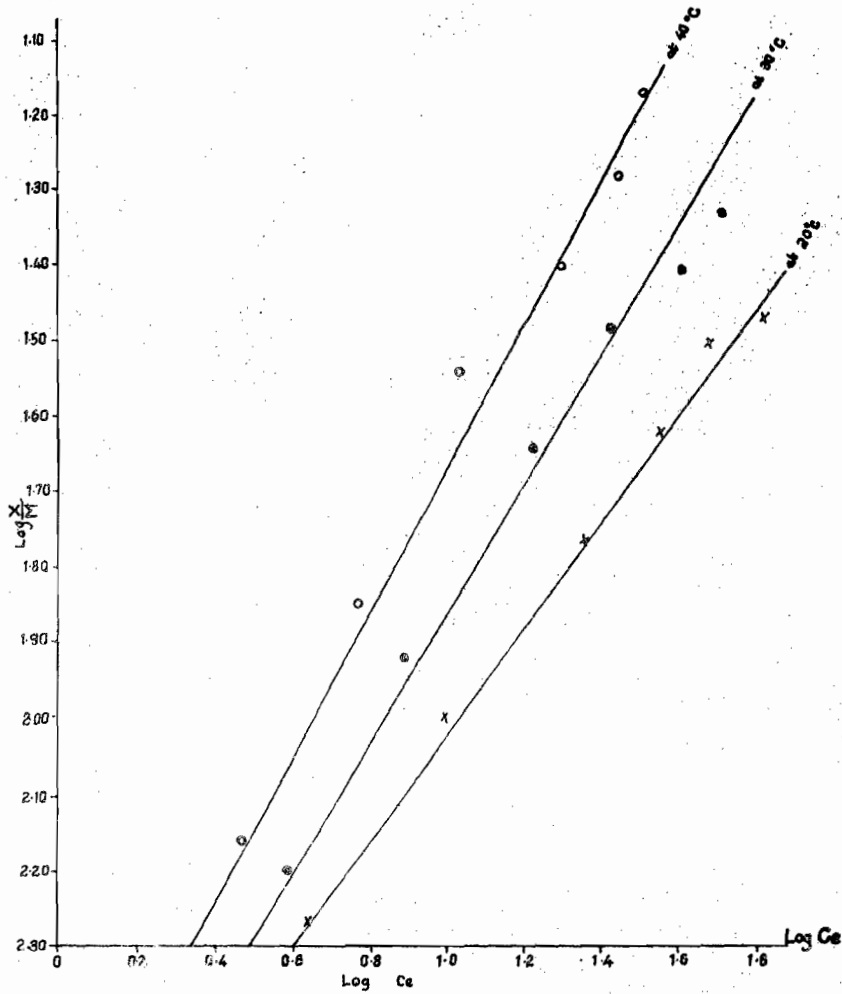


Fig. 5: Adsorption of Urea on Saw Dust Plot of $\text{Log } \frac{X}{M}$ vs $\text{Log } C_e$.
Freundlich Adsorption Isotherm.

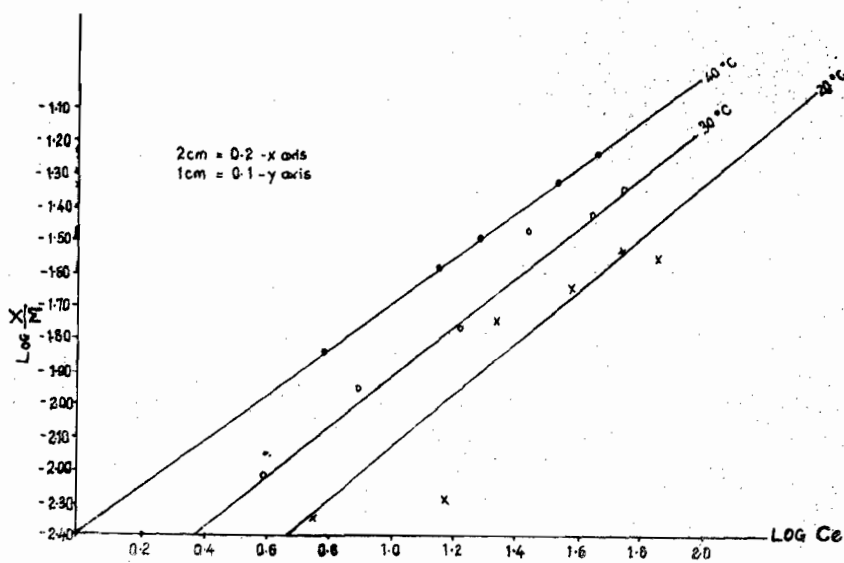


Fig. 6: FREUNDLICH ADSORPTION PLOT OF $\text{LOG } \frac{X}{M}$ VS $\text{LOG } C_e$ FOR MELAMINE ON SAW-DUST

RESULTS AND DISCUSSION

Adsorption rates

The experimental results showed that the adsorption of either urea or melamine on saw dust was not very fast since equilibrium was attained between 16 and 24 hours. As such an equilibrium time of 24h was adopted for the three different concentrations used. In comparison, further analysis of the results showed that 28.13%, 45.75%, and 56.25% by weight of urea were adsorbed by 10g saw-dust while 35.56%, 54.38% and 59.12% by weight of melamine were adsorbed by the same weight of saw-dust respectively at this equilibrium time (Fig. 1 & 2).

From the results above, it could be seen that increased adsorption of melamine and urea occurred with time and concentration. Also there was linearity in the relationship between percentage adsorbed and time of adsorption for both systems below 2 hours; under this time, the 1.5g/100cm³ concentration had the greatest slope and hence the highest percentage adsorbed.

Furthermore, it was observed that the melamine adsorbed was greater than the amount of urea adsorbed by saw-dust under the same conditions including concentrations. This could be attributed to the respective solubilities of the adsorbates. It has been found that the rate of adsorption from solutions depends to a large extent on the solubilities of the solutes in solution.¹⁵ Thus, more soluble salts are less adsorbed than the less soluble ones. This is in agreement with the observations of Sawzan El-Masry et al.¹⁵ on the adsorption of atropine and hyosine on magnesium trisilicate and the work of Khalil¹⁶ on the uptake of digoxin and digitoxin by some antiacids.

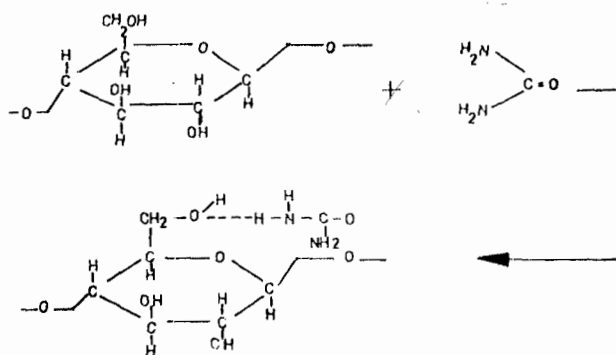
Also, owing to the heterogeneous nature of cellulose (Saw-dust), the results of modifications carried out in aqueous medium are expected to be affected by pore size, the crystalline - amorphous ratio, the degrees of orientation, and the size of the crystallites. However, it is believed that more of the reactions occur in the amorphous regions of cellulose.¹⁷ Cellulose reacts as a trihydric alcohol with one primary and two secondary hydroxyl groups

per glucose unit. These three reactive hydroxyl groups act as binding sites for adsorbates by formation of addition compounds in the case of surface reaction like sorption.¹⁷ Also because of the structure of cellulose (saw-dust), it is known to undergo both heterogeneous and homogeneous hydrolysis.

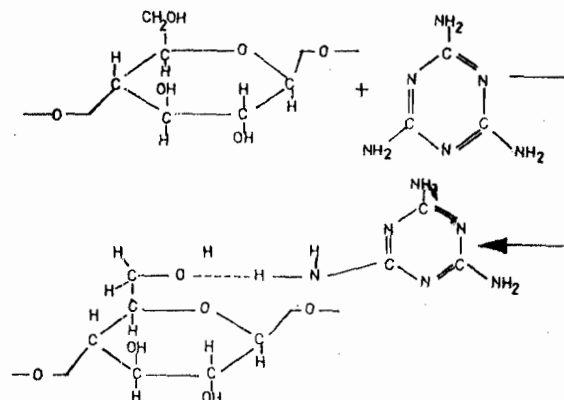
Heterogeneous hydrolysis reactions are known to take place with hydroxyls of the two types (primary and secondary), and the reaction is topochemical (micellar/heterogeneous). The quality of the submicroscopic structure determines the rate of reaction. In this type of reaction, the rate of reaction decreases as the reaction progresses to regions of high lateral order. There is an initial rapid rate which gradually decreases to a levelling-off stage. This has been seen to occur with our systems.

Although the adsorption process of urea and melamine on saw-dust cannot be said to have been adequately understood, it is believed that attachment of the adsorbate molecules onto the adsorbent involves van der Waals bonding which is a physical adsorption process and also hydrogen bonding⁸ which is illustrated in chemical equations (a) and (b).

(a) Urea attachment to cellulose/sawdust by hydrogen bonding



(b) Melamine attachment to cellulose/sawdust by hydrogen bonding



The influence of temperature on adsorption

Data Treatment:- The variation in the uptake of urea and melamine at varying concentrations and fixed temperatures with time is shown in Figures 1 and 2. In nearly all cases, adsorption equilibrium was achieved between 16 and 24 hours. Evidently, the degree of adsorption of these adsorbates was found to be dependent on concentration and temperature.

These adsorption data were respectively subjected to Langmuir and Freundlich's treatment. According to the modified Langmuir equation:

$$\frac{C_e}{y} = \frac{C_e}{y_m} + \frac{1}{by_m} \quad \text{..... (1)}$$

where y is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium concentration. C_e of the adsorbate at a given temperature while y_m is the amount of adsorbate that 1g adsorbent can take up when a monolayer coverage is complete, with b being the ratio K_1/K_2 and is constant. K_1 and K_2 are the rate constants for the forward and backward reactions respectively. The values y_m and b for the various isotherms in Figures 3 and 4 can be seen in Table 1.

Also Freundlich's adsorption isotherm equation gives

$$\text{Log} \frac{X}{M} = \text{Log} K + 1/n \text{ log } C_e \quad \text{..... (2)}$$

X is the amount of solute adsorbed by a given mass M of adsorbent while K represents the amount of adsorbate per unit weight of adsorbent and at unit adsorbate concentration while n , derivable from the slope, represents the amount of adsorbate adsorbed for a given concentration change. The Freundlich's Isotherms for the various systems are shown in Figures 5 and 6. The values of K and n for the various Isotherms are shown in Table 1.

From the result shown in Figures 3-6 and Table 1, it could be seen that the values of y_m , the adsorptive capacity of the adsorbent for the adsorbate, increased with increase in temperature for nearly all cases with Langmuir isotherm. Also the values of b related to the binding force between the adsorbent and adsorbate increased with increasing temperature

except for the case of urea adsorption on saw-dust at 40°C. At ambient temperature for instance, the value of y_m for urea on saw-dust was 5.88×10^{-2} mg/mg while that at 40°C was 25×10^{-2} mg/mg; however with melamine on saw-dust, the values of y_m at ambient and at 40°C were 7.33×10^{-2} and 12.50×10^{-2} mg/mg respectively. Also comparing the values of y_m for the adsorption of urea on saw-dust with the adsorption of melamine on saw-dust, it could be clearly seen that melamine had stronger affinity for saw-dust than urea (Table 1).

With the Freundlich's isotherms, almost the same trend was observed. The values of K , adsorptive capacities, increased with temperature for all cases investigated (Table 1). At ambient temperature the value of K was higher for the adsorption of urea on saw-dust than it was for melamine on saw-dust but at the higher temperatures of 30°C and 40°C the values of K for the adsorption of melamine on saw-dust became higher than those of urea on saw-dust. The increase in K value with increase in temperature for Freundlich's adsorption isotherm agrees with that of Langmuir.

Also the value of n decreased with increase in temperature for the adsorption of urea on saw-dust whereas it increased with increase in temperature for the adsorption of melamine on saw-dust as in the case of Langmuir adsorption isotherm. This observation could be explained with the following reason.

Although it has been proved that adsorption processes are exothermic reactions and as such adsorption should decrease with increase in temperature due to the negative entropy of activation¹⁹, this observation has not been found to be so in this case. It is believed that little adsorption took place at room temperature due to the strong solute solvent-interaction. It is known that urea and melamine are hydrophilic substances as a result of their carbonyl and amino groups. This property makes them to form hydrogen bonds with water molecules and, consequently, adsorption from solution is rendered more difficult. With increase in temperature, it is likely that these bonds are broken making the solute available for adsorption onto the adsorbent.

This adsorption of the solute onto the adsorbent is enhanced at higher temperatures by the fact that the solute and the adsorbent are like materials and as soon as the solvent-solute bonds are broken the adsorbent affinity for adsorbate increases making it possible for more adsorbate to be adsorbed onto the adsorbent¹³. Also urea and melamine are known to be cationic agents. These cations are known to adsorb readily at cell membrane structures in a non-specific manner, leading to cell lysis²⁰.

Another important factor that might be responsible for the increase in adsorption with increase in temperature is the swelling phenomenon of saw-dust. It has been established from previous work that saw-dust swells in water exhibiting high swell index²¹. This swelling phenomenon is enhanced by increase in temperature which enables the pores of the cellulose material to open up for more adsorption rather than capillary condensation or multi-layer formation to take place¹⁷. From the above observation it could be seen that the adsorption of urea and melamine onto saw-dust is an endothermic process. This observation is in agreement with the work of R. E. White et al.²² on the reaction of soluble phosphate with solid soils.

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