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### Short Communication

## The adsorption of urea on clays

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As part of a programme of examining adsorbers and ion exchangers for the catabolites and excess electrolytes in uraemic blood (Ioakim and Rosen, 1976; Grynepas et al., 1984) we have sought an adsorber for urea other than oxidized starch (Giordano et al., 1968). The drawbacks to the use of oxystarch are that it is a relatively expensive material and that it supports bacterial growth. Having been struck by Weiss's account in "A secret of Chinese porcelain manufacture" (Weiss, 1962) of how for centuries Chinese porcelain makers kept kaolinite stock in their back gardens and had their families urinate on it to improve its physical properties, we thought it worth while to examine the adsorption of urea onto kaolinite and other minerals. Although it has been shown by Weiss et al. (1963) and others (e.g. Olejnik et al., 1970) that urea can intercalate into clays, altering the layer spacings, the adsorption of urea on these materials seems not to have been studied. We find that there is significant adsorption of urea onto well-ordered and highly crystalline kaolinites, but not onto the other minerals we have used. We have not yet found adsorptive capacities as high as that of oxystarch, but possibilities exist of enhancing the capacities we have measured.

As possible adsorbents for urea we have examined various hydrous aluminium silicates (clays), hydrous magnesium silicate, micas and zeolites, selected because of their availability. The individual species are listed in Table 1. In all cases the samples were clean and powdered (except for the sepiolite which is fibrous, not powdery) and were washed in distilled water. In the initial experiments we merely sought evidence of some adsorption and used the minerals after they had been powdered to about the same size. For the later experiments, samples of the first 4 species of kaolinites in Table 1 were prepared in the following manner. A 5–10 g sample was dispersed in either water or an electrolyte solution specified below using 10 ml · g<sup>-1</sup>

TABLE 1

ADSORPTION OF UREA FROM SOLUTION IN DISTILLED WATER AT 18°C ONTO VARIOUS MINERALS

Figures give mg of urea adsorbed per gram of mineral. Blanks indicate less than 0.04 mg·g<sup>-1</sup> adsorbed.

Mineral	Remarks	Urea concentration	
		1 g·l <sup>-1</sup>	12 g·l <sup>-1</sup>
<i>Hydrous aluminium silicates</i>			
Kaolinites Pugu K	Highly crystalline	0.39	2.09
Specwhite	Commercial product <sup>a</sup>	0.18	1.49
Grade B	Commercial product <sup>a</sup>	0.24	1.63
Grade E	Commercial product <sup>a</sup>	0.16	1.22
Supreme	Commercial product <sup>a</sup>	—	—
Georgia I	Well crystallized	0.15	2.16
Georgia II	Poorly crystallized	—	—
Dickite		—	—
Metakaolinite	Pugu K after heating to 800°C	—	—
Montmorillonite		—	—
Fullers earth	Ca-bentonite	—	0.45
Halloysite		—	—
<i>Hydrous magnesium silicate</i>			
Sepiolite	Fibrous	—	—
<i>Micas</i>			
Illite		—	—
Muscovite		—	0.65
<i>Zeolite</i>			
Zeolite X	Synthesized at Imperial College	—	—
Ion sieve (Linde A)	Commercial product <sup>b</sup>	—	—

<sup>a</sup> English China Clays p.l.c.

<sup>b</sup> Union Carbide.

of kaolinite, and the suspension was left on magnetic stirring for 24 h at room temperature, after which it was centrifuged and the sediment oven-dried at 100°C for 3 days. The dried clay was powdered, resuspended in a volume of 3 ml of the same liquid per gram of kaolinite, and an ultrasonic probe was sunk about 1 cm into the suspension which was then sonicated at a power output of 1 W for 4 h. This treatment sized down the mineral and produced a stable sol which did not sediment within two weeks at room temperature. We assumed that this uniform treatment resulted in samples with grain size (and surface area) sufficiently close for our purposes. Aliquots of the sol were dispensed for the adsorption experiments.

In all cases, the minerals were dispersed in the proportion of 1 g in 10 ml of urea solution at the required concentrations after taking into account the volume of liquid in the aliquot, in tubes containing glass balls. The tubes were sealed and immersed in a constant temperature bath (18°C or 37°C) for 24 h with shaking. Thereafter the

tubes were centrifuged at 400 rpm for 30 min. Aliquots of the clear supernatant solution were drawn for urea estimation.

Urea adsorption was estimated from concentration differences between the original solution and the equilibrated supernatant solution. Although the differences were in some cases up to about 30% of the original values they were more often very small and the estimation of adsorption thus open to significant error. In attempting to improve final accuracy, the urea concentrations were measured by two separate and independent methods. The first used *p*-dimethylaminobenzaldehyde (Watt and Chrisp, 1954) and spectrophotometric measurement at 402 nm. The second used the Technicon Autoanalyzer system of blood urea determination involving urease and nicotinamide adenine dinucleotide (NADH<sub>2</sub>) with spectrophotometric measurement at 340 nm. The Autoanalyzer measurements were made on the automated apparatus in the Clinical Biochemistry Department of the Brompton Hospital, London, by courtesy of Mr. S. Nagarajah. For every experiment, three parallel samples were measured by each method, and each sample in duplicate, so that final urea concentrations were determined from the average of 12 measurements. These groups of measurements usually had a standard error of about 2% and a total spread of values of not more than 5% of the overall mean.

Adsorption of urea onto the full range of minerals was studied only from solutions of urea in distilled water. Experiments concerned with adsorption onto the kaolinites which were studied in more detail also used other solutions of urea. One, designated U-solution, was of urea in an electrolyte solution with the cation concentrations approximately matching those of uraemic blood (NaCl 133.0 mM, KCl 6.0 mM, CaCl<sub>2</sub> 1.75 mM and MgCl<sub>2</sub> 1.0 mM) (Grynepas et al., 1984). Additionally, urea was used in buffered solutions (Tris), either Tris alone in distilled water or Tris in U-solution, in each case at a concentration of 50 mM, giving pH 7.4 at 37°C.

The results of the preliminary survey of urea adsorption is shown in Table 1. The minerals at this stage were in a relatively crude form, having been merely powdered and well washed in distilled water but without having been otherwise treated or separated into fractions according to particle size. The clear indication that significant adsorption occurred only onto clays of highly crystalline kaolinites led us to concentrate further experiments on Pugu K and on Specwhite, Grade B and Grade E, the last 3 being commercial kaolinites available from English China Clays p.l.c. and the former having been obtained by us in kilogram quantities through the offices of the Tanzanian High Commission in London. It might also have been worth further examining Georgia Well Crystallized kaolinite but we were unable to obtain an adequate quantity of it.

Adsorption of urea onto the 4 crystalline kaolinites after sonication was measured by the methods described above from distilled water and from solutions of urea in U electrolyte (see above) at 18°C and 37°C. Urea concentrations were in the range up to 12 g · l<sup>-1</sup> (0.2 M). The adsorption isotherms were of the Freundlich type, viz. the weight of urea adsorbed, *W*, was given by an equation of the form  $W = aC^b$  where *C* is the urea concentration and *a* and *b* are constants. The example shown in Fig. 1 was typical and in all cases we found *b* > 1, making the curve concave upwards. In

this respect the behaviour of all 4 clays was similar, but whereas for Specwhite and Grades B and E kaolinites, the amount of urea adsorbed fell by about two-thirds on raising the temperature from 18°C to 37°C, for Pugu K there was practically no effect of temperature in this range (Table 2).

Since Pugu K was the kaolinite with most promise for eventual use in the treatment of uraemia it was the only one used in the final set of experiments. Since the adsorption properties of kaolinites can be altered by intercalating molecules into the crystalline structure and since small very polar molecules like urea are convenient intercalating agents (Olejnik et al., 1970), we treated samples of Pugu K by soaking them in urea solutions. The samples were dispersed (1 g to 10 ml) in solutions of 0.5 M or 1 M urea in Tris-U solution (see above) and left with magnetic stirring at room temperature for 24 h. The dispersions were sonicated at a sonicator output of 1 W for 4 h, although one sample in 1 M urea solution was left unsonicated. The dispersions were then shaken for 100 h at 37°C and thoroughly washed until no detectable urea appeared in the supernatant solution, after which they were dried and then treated as before for adsorption measurements.

The results of the adsorption experiments of urea onto the treated Pugu K kaolinite are shown in Table 2. Treatment with concentrated urea solution significantly increased the adsorptive capacity of the material although there are no

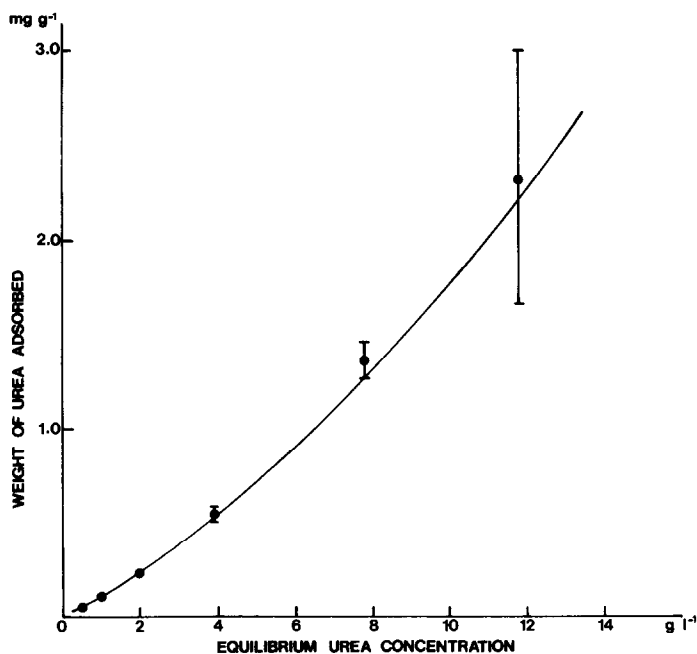


Fig. 1. Adsorption of urea from 0.1 M Tris solution pH 7.4 at 37°C onto Pugu K kaolinite. The clay was washed and sonicated before being dispersed in the proportion 1 g in 10 ml of urea solution. The line is drawn according to the calculated best-fit Freundlich isotherm  $W = 0.100 C^{1.243}$ .

TABLE 2  
 ADSORPTION OF UREA ONTO PUGU K KAOLINITE IN VARIOUS CONDITIONS

Figures give mg of urea adsorbed per g of clay.

Pretreatment	Conditions			Urea concentration	
	Solvent	pH	Temp.(°C)	1 g·l <sup>-1</sup>	4 g·l <sup>-1</sup>
Thorough washing in water	Water	~ 6	18	0.39	-
<i>and</i> sonicated in solvent	Water	~ 6	18	-	2.15
	Water	~ 6	37	-	2.29
	U solution	~ 6	18	-	2.44
	U solution	~ 6	37	-	2.53
	Tris-U solution	7.4	37	1.74	2.76
<i>and</i> (a) sonicated in 0.5 M urea or (b) sonicated in 1.0 M urea or (c) 1.0 M urea, unsonicated	Tris-U solution	7.4	37	2.68	4.41
	Tris-U solution	7.4	37	2.31	5.14
	Tris-U solution	7.4	37	2.15	5.05

significant differences in amounts of material adsorbed between samples treated in 0.5 M or 1 M urea solutions or between samples sonicated or unsonicated.

The average adsorption we have obtained of 2.38 mg urea onto 1 g of treated Pugu K kaolinite from a urea concentration of  $1 \text{ g} \cdot 1^{-1}$  is significantly less than the adsorption from the same concentration of 7.0 mg urea onto 1 g of oxidized starch (Giordano et al., 1976). However, the considerable increase in adsorptive capacity of Pugu K after treatment by soaking in concentrated urea solution demonstrates the changes which can be brought about by simple procedures. It is probable that adsorption kaolinites can best be increased by the action of intercalated species ("guest molecules") in altering layer spacings and continued exploration of the variables offers the possibility of still further increase in absorptive capacity of Pugu K or of the development of urea adsorption in commoner kaolinite species. Among relevant variables which need to be explored are: grain size of mineral (clay), intercalating species other than urea (e.g. formamide, acetamide, dimethyl sulphoxide (Olejnik et al., 1970)), the concentration of intercalating species in the treating solution, and pH and temperature of the treating solution.

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