

THE ADSORPTION OF D-GLUCOSE AND GLUCANS BY MAGNETIC CELLULOSIC AND OTHER MAGNETIC FORMS OF HYDROUS TITANIUM(IV) OXIDE

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ABSTRACT

A more-effective means of activating cellulose than hitherto reported has been devised for the abstraction of carbohydrates from solution. Cellulose coated with hydrous titanium(IV) oxide readily adsorbs branched polysaccharides such as glycogen (e.g. a coated cellulose containing 4.5% of titanium will adsorb 0.52 mg of glycogen/mg of titanium) and has a low affinity for monosaccharides. The hydrous oxide, as a dried powder, had a lower maximum adsorption (0.08 mg of glycogen and 0.02 mg of D-glucose/mg of titanium) showing the beneficial effect of its coating on cellulose. Conversely, freshly prepared hydrous titanium(IV) oxide, which had been neither washed nor dried, had a greater maximum adsorption of glycogen (4.46 mg/mg of titanium) whilst the generation of the hydrous oxide in solutions of glycogen further increased the maximum adsorption of glycogen (8.40 mg/mg of titanium). Magnetic iron oxide coated with hydrous titanium(IV) oxide retains all the adsorption properties of the freshly prepared hydrous titanium(IV) oxide and improves the handling and sedimentation properties of the material, including its response to magnets.

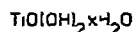
INTRODUCTION

Transition metals such as titanium, iron, tin, vanadium, and zirconium have been used to activate the surfaces of various matrices such as cellulose and nylon¹⁻³, glass^{1,2,4}, alginate⁵, chitin, and Celite⁵, and poly(Λ -acryloyl-4- and -5-amino-salicylic acids)⁶, to give derivatives to which enzymes^{1,2,4-6} and antibiotics³ can be attached. New techniques have been developed which use the oxides and hydroxides of the transition metals as a means of binding and insolubilising amino acids, peptides, and enzymes^{7,8}. These oxides and hydroxides also bind a number of organic compounds, including sodium dodecyl sulphate⁹, formic acid¹⁰, and polystyrene¹¹.

Since the discovery^{1,2} of a hydroxide of titanium(IV), a number of structures have been postulated for titanium hydroxide precipitated by hydrolysing solutions of titanium(IV) compounds^{1,3-17}. A comprehensive study of the fresh precipitates^{1,2}

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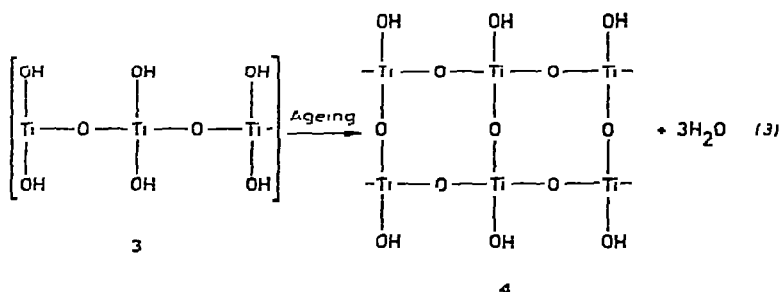
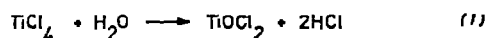
indicated that the ratio of hydroxyl groups to titanium remained constant at a value close to 2.1 for precipitates kept under a layer of mother liquor, but decreased to a new constant ratio (1.1) after 15 days when the precipitates were stored in air. From these results, and those obtained from i.r. spectroscopy¹⁸ which indicated the presence



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of chains and the absence of any titanium-oxygen double bonds, it was concluded¹⁵ that the only hydroxide precipitated from aqueous titanium(IV) chloride solutions has the more thermodynamically stable¹⁹ structure 1 and not 2. Equations 1-3 show the initial hydrolysis reaction, the subsequent neutralisation reaction which leads to precipitation, and the decrease in the ratio of hydroxyl groups to titanium from 2.1 for the fresh precipitate (3) to 1.1 for the aged precipitate (4), respectively.

Since water molecules become bound by polar ionic forces or partial covalent bonds to the titanium atoms of hydrous titanium(IV) oxide to complete the octahedral co-ordination, but are replaceable by other ligands, it seemed likely that the chelation of carbohydrates by hydrous titanium(IV) oxides could occur. We now report on the adsorption of D-glucose and some polysaccharides by hydrous titanium(IV) oxides alone or as coatings on various supports. A more-detailed description of the nature of hydrous titanium(IV) oxide and its binding characteristics has been reported⁷.

EXPERIMENTAL AND RESULTS

Preparation of solids used in adsorption studies — (a) Hydrous titanium(IV) oxide coated on cellulose

Ti-Cellulose A A mixture of titanium(IV) chloride ($\sim 15\%$ w/v TiCl_4 in 15% w/v hydrochloric acid, B D H, 15 ml) and microcrystalline cellulose (Type 19, Sigma Chemical Co Ltd, 1.5 g) was stirred to produce a uniform slurry, then dried as a thin layer in an oven at 45° for 18 h, and ground to a powder

Ti-Cellulose B Ti-Cellulose A was washed with water until acid-free, and then suspended in water (25 ml). The amount of solid in the suspension was determined by drying an aliquot of the suspension in an oven at 45° for 18 h

Ti-Cellulose C The suspension containing Ti-Cellulose B was dried in an oven at 45° for 18 h, and the resulting solid was ground to a powder

Ti-Cellulose D Titanium(IV) chloride solution (30 ml) was added to microcrystalline cellulose (3.0 g) and the suspension stirred for 30 min. After removal of the supernatant solution, the solid was washed with water until acid-free, dried in an oven at 45° for 18 h and ground to a powder

Ti-Cellulose E Titanium(IV) chloride solutions (0.2–15 ml) were diluted to 15 ml with 15% hydrochloric acid and added to samples of microcrystalline cellulose (1.5 g). These suspensions were stirred for 30 min, and then neutralised to pH 7.0 with ammonium hydroxide solution (concentrated until pH 5.5–6.5, then M). The solids were collected, washed with water (4×25 ml), dried in an oven at 45° for 18 h, and ground to a powder

Ti-Cellulose F Cellulose was treated as for the production of Ti-Cellulose E (using undiluted titanium(IV) chloride solution), but the supernatant solution was removed prior to neutralisation

(b) Hydrous titanium(IV) oxides Samples of hydrous titanium(IV) oxides, prepared by neutralising titanium(IV) chloride solution (15 ml) with ammonium hydroxide solution to pH 7.0 as previously described, were washed with water (4×25 ml) and then suspended in water (25 ml). These suspensions were either used immediately, freeze-dried, or oven-dried at 45° for 18 h. The resulting solids were ground to powders

Hydrous titanium(IV) oxide was also prepared by transferring titanium(IV) chloride (Hopkin and Williams, 10 μl) to stoppered tubes in a dry atmosphere, to minimise atmospheric hydrolysis. Water (1000 μl) was added, the solution neutralised with ammonium hydroxide solution (M) by titration to a known pH in the range 1 to 9 and the solid used immediately for adsorption studies

(c) Hydrous titanium(IV) oxide coated on magnetic iron oxide Magnetic iron oxide (Fe_3O_4 , Fisons, 40 mg) was treated with titanium(IV) chloride (10 μl or 20 μl), followed by hydrolysis with water and neutralisation to a known pH as described for the freshly prepared hydrous titanium(IV) oxide

Analysis of titanium compounds — The titanium was determined by conversion

(muffle furnace, 700°, to constant weight) into titanium(IV) dioxide. Hydrous titanium(IV) oxide and cellulose, and a mixture of the two, were similarly treated to ensure that complete conversion into titanium(IV) dioxide was obtained with no residue remaining from the cellulose (Table I). The percentage of water in the "dry" hydrous titanium(IV) oxides was also estimated from the loss in weight at 700°. The resulting value is the sum of adsorbed water molecules and water obtained by converting hydroxyl groups into the anhydrous titanium(IV) dioxide.

TABLE I

CALCINATION OF CELLULOSE AND HYDROUS TITANIUM(IV) OXIDE

<i>Solid</i>	<i>Initial weight (g)</i>	<i>Final weight (g)</i>
Cellulose	0.0517	0.0012
Hydrous titanium(IV) oxide	0.0518	0.0415
Hydrous titanium(IV) oxide + cellulose	0.0516 + 0.0517	0.0433

Adsorption of carbohydrates onto Ti-Celluloses — Samples (25 mg) of Ti-cellulose suspended in water (1000 μ l) or aliquots of the suspensions (500 μ l diluted with 500 μ l of water) were treated in duplicate with aqueous solutions (400 μ l, 1 mg/ml) of D-glucose, glycogen (from Shellfish, type II, Sigma Chemical Co.), and starch (Viscosol 240' soluble starch, St. Anne's Board Mill Co. Ltd., Bristol). The suspensions were stirred magnetically for 18 h at 20°, after which the supernatant solutions were removed, and assayed for carbohydrate by the cysteine-sulphuric acid method²⁰. Control solutions without the Ti-Cellulose and control suspensions without carbohydrate were used. The results are given in Table II.

The effect of concentration of the carbohydrate on the adsorption was studied by using glycogen solutions (1.4 ml) in the range 0–10 mg/ml, and two solids from the Ti-Cellulose E range (containing 4.5 and 21.1% of titanium) (Fig. 1).

Adsorption of carbohydrates onto hydrous titanium(IV) oxides — The adsorption of carbohydrates onto freeze-dried and oven-dried hydrous titanium(IV) oxides was investigated as described for the Ti-Cellulose. The results are recorded in Fig. 1 and Table III. No results could be obtained for the prepared suspension of hydrous titanium(IV) oxide, due to its colloidal nature after stirring with carbohydrate solution for 18 h.

For freshly prepared hydrous titanium(IV) oxide, after removal of the supernatant solution, aqueous glycogen (20 mg/ml, 2000 μ l) was added and after thorough mixing and centrifugation, the supernatant solution was removed and assayed for carbohydrate (Fig. 2).

A similar experiment was performed with freshly prepared hydrous titanium(IV) oxide using carbohydrate solutions (2000 μ l) to hydrolyse the titanium(IV) chloride in place of the water added prior to neutralisation (Equation 1). Various ratios of titanium(IV) chloride to carbohydrate concentration (50 μ l, 1 mg

TABLE II

ADSORPTION OF CARBOHYDRATES ONTO Ti CELLULOSES

Ti-Cellulose type	Titanium content (%)	Blank value ^{a,2} (μg of glucose/ml)	Carbohydrate adsorbed (%)		
			D Glucose	Glycogen	Starch
A	—	260	24.3	15.2	0.0
B	—	18	0.0	85.0	93.0
C	—	34	1.5	89.5	89.0
D	—	368	0.0	0.0	0.0
E	21.1	0	42.1	99.3	55.3
E	16.9	4	37.8	96.9	51.5
E	4.5	2	33.2	91.9	24.0
E	3.9	246	18.4	34.5	45.8
E	3.2	202	20.9	40.1	27.3
E	2.4	86	6.4	31.3	9.1
E	1.0	68	2.4	24.4	10.0
E	0.7	68	1.9	21.5	14.0
E	0.0	252	0.0	0.0	0.0
F	—	44	4.1	17.1	7.5

Carbohydrate concentration of the supernatant of control suspensions (no carbohydrate added). These values were taken into account when calculating the adsorption of carbohydrate.

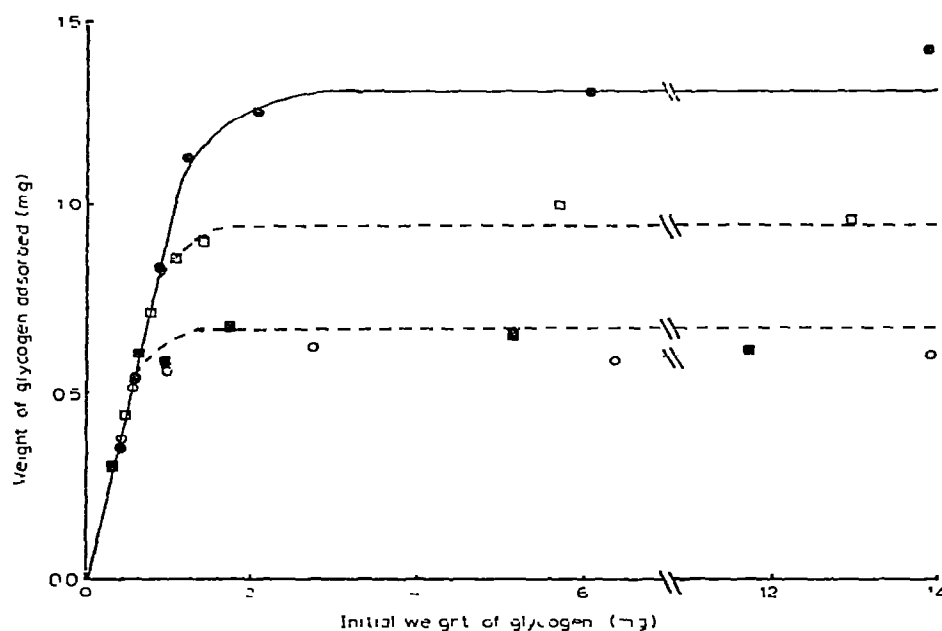


Fig. 1 Effect of glycogen concentration on the adsorption of glycogen by hydrous titanium(IV) oxides. Ti-Cellulose E (21.1% Ti) —●—●—, Ti-Cellulose E (4.5% Ti), ○ ○, oven-dried hydrous oxide (21.3% water), —□—□—, and freeze-dried hydrous oxide (18.4% water) —■—■—.

TABLE III

EFFECT OF CARBOHYDRATE CONCENTRATION ON THE ADSORPTION OF CARBOHYDRATES BY OVEN DRIED HYDROUS TITANIUM(IV) OXIDE

Concentration ($\mu\text{g/ml}$)	D-Glucose adsorption ($\mu\text{g/mg of Ti}$)	Percent adsorbed	Concentration ($\mu\text{g/ml}$)	Starch adsorption ($\mu\text{g/mg of Ti}$)	Percent adsorbed
74	6.5	71.2	68	7.3	90.2
224	16.5	60.1	158	16.0	82.4
300	25.3	68.6	196	24.2	100.0
373	24.3	52.9	328	38.0	94.1

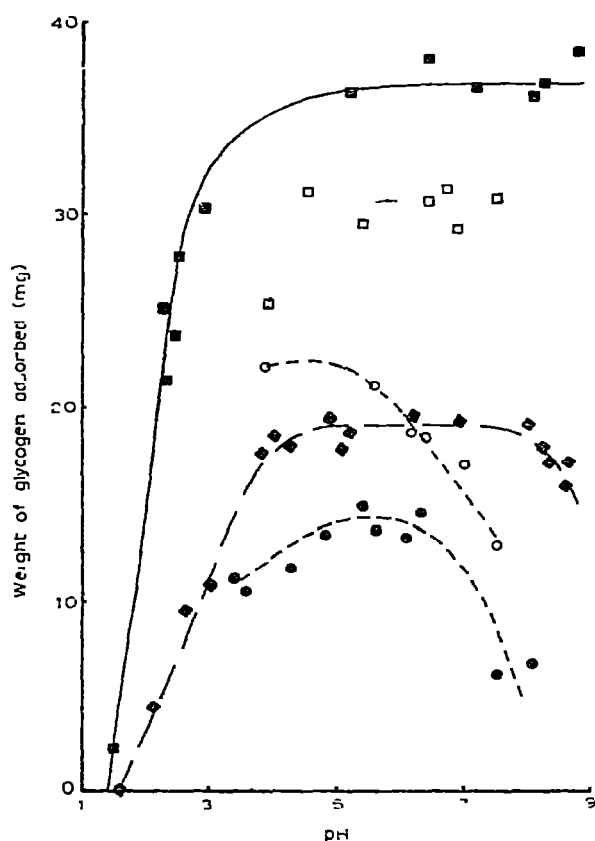


Fig 2 Effect of final pH of neutralisation of titanium(IV) chloride on the adsorption of glycogen (20 mg/ml in water, 2 ml) by the resultant hydrus titanium(IV) oxide. Titanium(IV) chloride (10 μl) using water hydrolysis, —◆—◆—, titanium(IV) chloride (10 μl) using glycogen solution hydrolysis, —■—■—, hydrus titanium(IV) oxide-coated iron oxide (10 μl of TiCl_4) using water hydrolysis, —●—●—, hydrus titanium(IV) oxide-coated iron oxide (20 μl of TiCl_4) using water hydrolysis, —○—○— and hydrus titanium(IV) oxide-coated iron oxide (10 μl of TiCl_4) using glycogen hydrolysis, —□—□—

of glycogen/ml, 50 μ l 10 mg of glycogen/ml, 10 μ l 20 mg of glycogen/ml, and 10 μ l 20 mg of D-glucose/ml) were used to saturate the hydrous titanium(IV) oxide with carbohydrate (Fig 3). The adsorption of D-glucose was 0.09 mg/mg of titanium.

Adsorption of carbohydrates onto hydrous titanium(IV) oxide-coated magnetic iron oxide — After removal of the supernatant solution, aqueous glycogen (20 mg/ml, 2000 μ l) was added as described above, to the freshly prepared hydrous titanium(IV) oxide-coated magnetic iron oxides and, after thorough mixing, the supernatant solution was assayed for carbohydrate content (Fig 2).

A similar experiment was performed with the hydrous titanium(IV) oxide-coated iron oxide prepared from 40 mg of magnetic iron oxide and 10 μ l of titanium(IV) chloride, but using aqueous glycogen (20 mg/ml, 2000 μ l) to hydrolyse the titanium(IV) chloride (Equation 1) in place of the water prior to neutralisation (Fig 2).

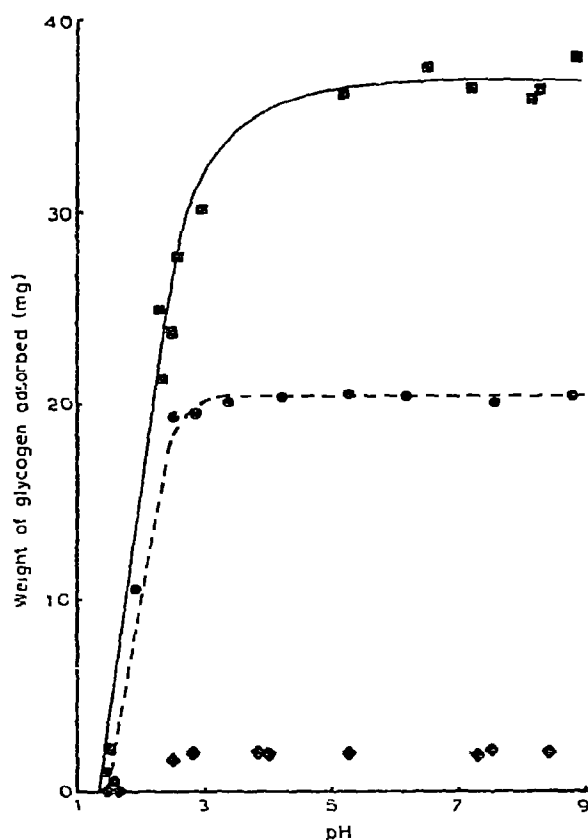


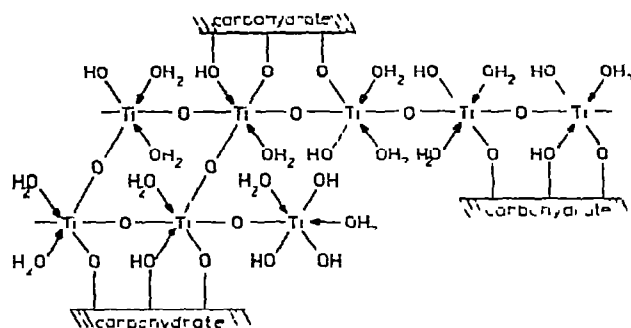
Fig 3 Effect of final pH of neutralisation of titanium(IV) chloride on the adsorption of glycogen by the resultant hydrous titanium(IV) oxide using glycogen solution (2.0 ml) hydrolysis TiCl_4 (50 μ l) and glycogen (1 mg/ml) \blacklozenge \blacklozenge , TiCl_4 (50 μ l) and glycogen (10 mg/ml) $-\bullet-\bullet-$ and TiCl_4 (10 μ l) and glycogen (20 mg/ml), $-\blacksquare-\blacksquare-$

DISCUSSION

In titanium(IV) chloride, the titanium atoms are tetrahedrally co-ordinated but hydrolysis leads to compounds that involve octahedral co-ordination. The ligands can be chlorine atoms (at low pH, but less likely as the pH approaches neutrality), water molecules, or hydroxyl-containing compounds³. When water molecules act as ligands, a lone pair of electrons from the oxygen co-ordinates to the metal atom. This situation is more likely for transition metals than binding solely by the dipolar action of water molecules. As the pH of the system rises, removal of a proton from the water molecule leads to the formation of a covalent bond between the resulting hydroxyl group and the titanium atom. At high pH, all water molecules present as ligands will have lost a proton to produce the titanate anion, but with the conditions used in the system under investigation the formation of this anion is not favoured.

Hydroxyl-containing compounds act as ligands in a similar manner, by appropriate formation of co-ordinate or covalent bonds. Some glycols are very efficient ligands for transition metals, replacing two of the ligand positions to form ring compounds (chelates), if the glycol molecule has unfavourably arranged hydroxyl groups, only non-ring compounds can be formed. Titanium compounds have been extensively used as cross-linking agents for polymeric polyols^{21, 22}. The titanium atoms in these materials are hexa-co-ordinated, linking two or more chains *via* four covalent and two co-ordinate bonds, and not by simple trans esterification of tetrafunctional titanium^{23, 24}. When titanium compounds form complexes with carbohydrates, solvolysis of the titanium-ligand bond gives titanium-oxygen-type bonds. Cellulose has HO-2 and HO-3 available for chelate formation, but HO-6 can only partake in non-ring complex formation. The Ti-Celluloses can be considered as a range starting with titanium(IV) activated cellulose³ (Ti-Cellulose A) and ending with hydrous titanium(IV) oxide-coated cellulose (Ti-Celluloses E), with the intermediate materials being considered as incompletely coated celluloses. Hence, when titanium(IV) chloride is mixed with cellulose and the acid, produced as a result of the hydrolysis (Equation 1), is removed by evaporation (Ti-Celluloses A, B, and C), washing (Ti-Cellulose D) or neutralisation with ammonia (Equation 2), products are obtained which can be represented by the schematic structure (5) with relatively more hydrous titanium(IV) oxide in the later preparations (*e.g.* Ti-Celluloses E).

The most-advantageous method of preparation of the titanium-cellulose materials was to use ammonia neutralisation. The products (Ti-Celluloses E) thus obtained neither decomposed in solution nor gave high "blank values" (Table II), provided the titanium content was $\geq 4.5\%$. Materials with lower titanium content gave unacceptably high "blank values", probably due to there being insufficient titanium available for cross-linking. That cross-linking of the cellulose had occurred in the formation of Ti-Celluloses E was evident from the fact that cellulose treated with acid in the absence of titanium (Ti-Cellulose E, zero titanium content) gave a high "blank value" (Table II), a phenomenon attributable to partial hydrolysis of the cellulose.



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When Ti-Cellulose E materials and oven- and freeze dried samples of hydrous titanium(IV) oxide were mixed with solutions of glycogen the polysaccharide was completely adsorbed up to a maximum for each solid used, thereafter, further increases in the initial concentration of glycogen only resulted in a higher final concentration after contact with the titanium compound. The relevant data are given in Figs 1-3 and Table IV. The highest glycogen adsorption values for these dry materials were exhibited by the Ti-Celluloses E. Within this series, a comparison was made under conditions which ensured complete saturation by D-glucose using two different materials (Ti-Cellulose E, 4.5% and 21.1% of Ti), and a higher maximum adsorption was obtained for the material with the lower titanium content. The material having the lowest titanium content (Ti-Cellulose E, 0.7% of Ti) appeared to have the highest maximum adsorption (1.58 mg/mg of Ti), but the high "blank value" made assessment under comparable conditions difficult. The higher maximum adsorptions

TABLE IV

MAXIMUM ADSORPTION OF GLYCOGEN BY HYDROUS TITANIUM(IV) OXIDES AND HYDROUS TITANIUM(IV) OXIDE-COATED CELLULOSE AND MAGNETIC IRON OXIDE

<i>Compound</i>	<i>Maximum adsorption (mg of glycogen/mg of titanium)</i>
Ti Cellulose E (4.5% Ti)	0.52
Ti Cellulose E (21.1% Ti)	0.24
Hydrous titanium(IV) oxide (oven dried, 21.3% of water)	0.08
Hydrous titanium(IV) oxide (freeze dried, 18.4% of water)	0.05
Hydrous titanium(IV) oxide (water hydrolysis)	4.46
Hydrous titanium(IV) oxide (glycogen solution hydrolysis)	8.40
Hydrous titanium(IV) oxide-coated magnetic iron oxide (10 μ l of TiCl_4) (water hydrolysis)	3.22
Hydrous titanium(IV) oxide-coated magnetic iron oxide (20 μ l of TiCl_4) (water hydrolysis)	2.62
Hydrous titanium(IV) oxide-coated magnetic iron oxide (10 μ l of TiCl_4) (glycogen solution hydrolysis)	7.06

associated with lower contents of titanium for these dry materials probably arises from greater densities of titanium per unit surface area, which allow more cross-linking of the hydrous titanium(IV) oxide chains (Equation 3 favouring 4), thereby resulting in fewer hydroxyl groups on the hydrous oxide being available for adsorptions of carbohydrate.

The dependence of glycogen adsorption on the number of available hydroxyl groups in the hydrous oxide structure can also be seen from the lower maximum adsorption obtained for the drier sample of hydrous titanium(IV) oxide (freeze-dried, 18.4% of water; oven-dried, 21.3% of water) (Fig. 1, Table IV). The oven-dried sample of hydrous titanium(IV) oxide contained more hydroxyl groups (shown by the greater loss in weight obtained on roasting to 700°) and therefore had less cross-linking between the hydrous oxide chains (Equation 3 favouring 3). Lower degrees of cross-linking between the hydrous-oxide chains not only implies that there are more hydroxyl groups available for replacement by carbohydrate hydroxyl groups, but that the structure of the hydrous oxide is more open, resulting in a greater accessibility to the carbohydrate molecules.

By using freshly precipitated hydrous titanium(IV) oxide, which had been neither washed nor dried, the maximum adsorption of glycogen (Fig. 3) was increased by a factor of 10 over the highest values obtained for the Ti-Cellulose materials (Table IV). This is because there is insufficient time for cross-links to form (almost completely structure 3), and the hydrous oxide is produced in a finely divided form, thereby having a large surface area:volume ratio. When glycogen solution was used, instead of water, to hydrolyse the titanium(IV) chloride (Equation 1) prior to neutralisation, the maximum adsorption was further increased by a factor of 2 (Table IV) due to some of the hydroxyl groups of the glycogen molecules hydrolysing the titanium-chlorine bonds. The mechanism of ligand replacement will also lead to adsorption after neutralisation.

The adsorption of carbohydrates by hydrous titanium(IV) oxide, either alone or as coatings on cellulose or magnetic iron oxide, most probably proceeds by a mechanism involving replacement of some ligands of the hydrous oxide^{3,7,8} (hydroxyl groups and water molecules) by hydroxyl groups from the carbohydrate molecules. Since D-glucose, glycogen, and starch possess vicinal-diol groups, it is probable that they form chelates (see 5). Whereas glycogen and starch can form only one chelate per D-glucose residue, a number of chelates can be formed with D-glucose. Complexation may also occur with single hydroxyl groups in the carbohydrate. Furthermore, the formation of one chelate bridge will result in a greater adsorption of polysaccharides than monosaccharides. This explains why the maximum adsorption for D-glucose (0.09 mg/mg of titanium) was ~90 times lower than that for glycogen (8.40 mg/mg of titanium) when the respective carbohydrate solutions were used in the initial hydrolysis of titanium(IV) chloride. The adsorption of D-glucose is, however, less subject to diffusion factors than that of glycogen, as shown by the difference in the maximum adsorption of D-glucose and glycogen for oven-dried hydrous titanium(IV) oxide (0.02 mg and 0.08 mg, respectively/mg of titanium, Tables III and IV),

which was much less than the difference obtained using the respective carbohydrate hydrolysis of titanium(IV) chloride.

Suspensions of the freshly prepared hydrous titanium(IV) oxide did not respond to centrifugation if the pH was <4.0 , due to their colloidal nature. Above pH 4.0, prolonged centrifugation ensured complete separation. Thus, the use of the hydrous oxide of zirconium, which does not exhibit such phenomena, has been advocated as an alternative⁸. However, this problem could be overcome by using the "dried" hydrous oxides or the Ti-Cellulose materials.

Freshly prepared hydrous titanium(IV) oxide adsorbs ammonium chloride to give a very gelatinous precipitate¹⁵, and for this reason, liquid titanium(IV) chloride was used in place of titanium(IV) chloride solutions in hydrochloric acid for making the freshly prepared hydrous oxide; the amount of ammonium chloride produced is thereby kept to a minimum. Magnetic iron oxide was also incorporated into the preparations in order to overcome these problems by increasing the bulk density of the hydrous oxide. By neutralising titanium(IV) chloride in the presence of the iron oxide, a coating of hydrous titanium(IV) oxide on the iron oxide was obtained. This incorporation resulted in improved precipitation and sedimentation characteristics, particularly when reinforced by a magnet. Separation by centrifugation was also greatly improved. The lower maximum adsorption of glycogen per unit weight of titanium obtained for materials containing iron oxide, compared with hydrous titanium(IV) oxide on its own, suggested that the hydrous oxide formed a coating around the iron oxide which involved some degree of bonding. This assumption is supported by the observation that when a magnet was held near a suspension of the coated iron oxide, all of the solid matter was attracted to the side of the tube and none was unaffected by the magnet.

The pH-dependence of the adsorption of glycogen by the hydrous titanium(IV) oxide-coated iron oxide (Fig. 1) can be explained in terms of the precipitation of the hydrous oxide. At low pH (~ 3.0), little hydrous oxide is precipitated, as can be seen by the colloidal nature of the solution during precipitation. As the pH of the solution is increased above 4.0, precipitation takes place, a coating is formed, and the adsorption increases. Increasing the pH above 7.0 causes complete precipitation of the hydrous oxide and the coating becomes thicker, allowing more cross-linking of the hydrous oxide chains to occur (Equation 3); this results in a lower surface area:volume ratio and a consequent lowering of the maximum adsorption. By increasing the amount of titanium(IV) chloride present, precipitation and coating formation starts at a lower pH because of the increased concentration of titanium(IV) species; however, the thickening of the coating and consequent dehydration (Equation 3) also starts at a lower pH, resulting in a shift in the maximum adsorption to a lower pH for higher titanium(IV) chloride:iron oxide ratios.

Thus, the use of hydrous titanium(IV) oxide-coated compounds, either in "dried" form (*e.g.*, Ti-Celluloses E) or freshly prepared (*e.g.*, hydrous titanium(IV) oxide-coated magnetic iron oxide), for adsorption of carbohydrates is superior to the use of titanium(IV)-activated matrices previously reported¹⁻², due to a more-

complete and permanent coverage of the matrix. The incorporation of magnetic iron oxide into hydrous titanium(IV) oxide produces a support which retains the properties of the hydrous oxide whilst possessing advantageous properties of recovery and handling. The adsorption of carbohydrates from solution by these means is to some extent analogous to the adsorption of polysaccharides by polyaromatic surfaces^{2,5}. However, the adsorption by hydrous titanium(IV) oxide is less specific than that by polyaromatic surfaces, as D-glucose is also adsorbed. Accordingly, it is envisaged that the hydrous titanium(IV) oxide will be used for purification purposes by removal of carbohydrate contamination, rather than the analytical process of affinity chromatography envisaged for the polyaromatic surfaces.

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