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# Adsorbents for the removal of humic acid from surface water based on modified porous zirconia and silica<sup>1</sup>

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## Abstract

In these investigations porous zirconia and silica particles have been modified with anion-exchanger functionalities of different ligand characteristics. Three different modifications were examined. Two modifications were based on polystyrene-coated particles with introduced quaternary amino groups, namely trimethylphenylammonium chloride and triethylphenylammonium chloride as the functional groups. The third modification was achieved by immobilising 4-amino-4',4"-bisdimethylaminotriphenylcarbinol, which is the 4-amino derivative of malachite green. These new high-performance ion-exchange adsorbents were then used to remove humic acid substances from river water, sampled at the well known wine growing district of the Barossa Valley, South Australia. Adsorption studies were performed in stirred tank systems with the adsorption behaviour monitored from the change in absorbance at 254 nm as function of time. After reaching saturation with the humic acid substances, the ion-exchange modified zirconia and silica particles could be readily regenerated with concentrated sodium chloride solutions.

## 1. Introduction

Humic substances are the product of incomplete decomposition of organic matter in an aquatic or terrestrial environment [1–3]. One major source for humic substances is lignin [4] (see Fig. 1). The humic substances can be subdivided in three groups, namely: humin, which represents insoluble components in aqueous solutions at all pH values; humic acids, which are soluble in alkaline to weakly acidic solutions but insoluble at or below pH 2.0 and

fulvic acids which are soluble in aqueous solutions at all pH values. The compositions of the humic substances vary with the nature of the original organic material and with the conditions which prevail during the decomposition. In the studies described in this publication, the main interest was focused on the humic acid components. The elemental analysis of 15 different samples of humic acid described in the literature [5] showed the following result for the average composition of humic acids: C:  $55.3 \pm 3.3\%$ , w/w (39.55 mol%); O:  $33.8 \pm 3.9\%$ , w/w (18.10 mol%); H:  $4.66 \pm 0.93\%$ , w/w (39.98 mol%); S:  $1.17 \pm 1.83\%$ , w/w (0.32 mol%); N:  $3.31 \pm 2.30\%$ , w/w (2.06 mol%).

The content of aromatic compounds in humic acid preparations as initially examined by oxidi-

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<sup>1</sup> Part CXXI in the series "High-performance liquid chromatography of amino acids, peptides and proteins". For Part CXL, see Ref. [25].

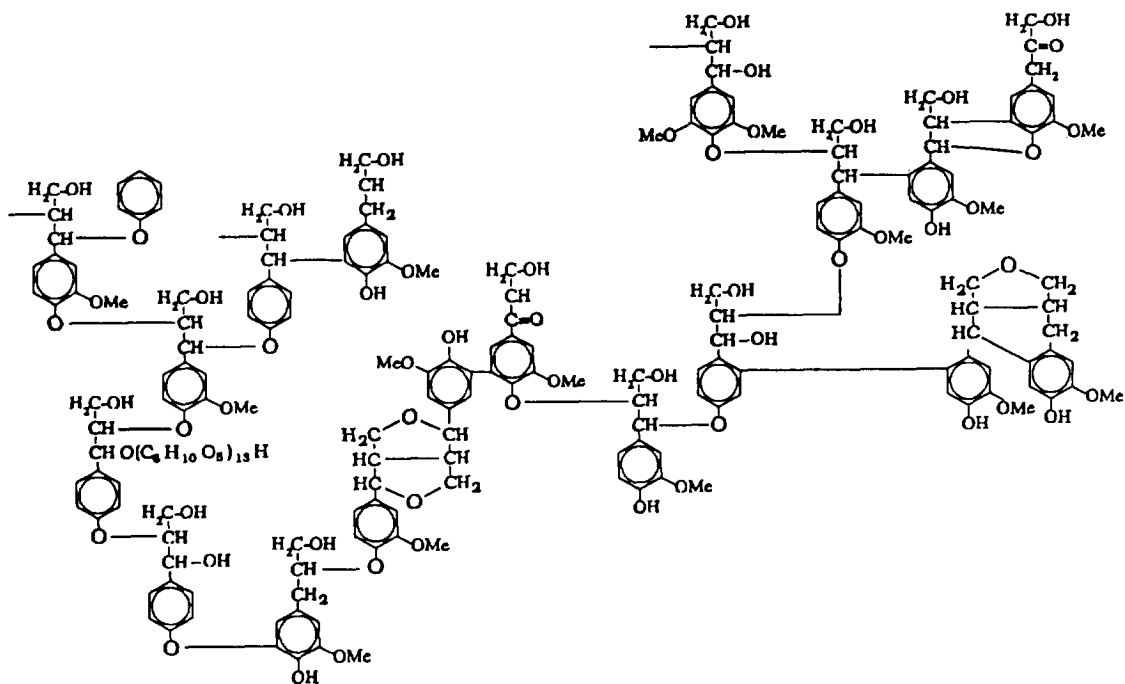


Fig. 1. Representative structure of coniferous lignin.

sation methods [6] was believed to be in the range of 95–100%. Recent studies, using cross-polarisation magic-angle spinning  $^{13}\text{C}$  NMR (CP-MAS-NMR) methods, have indicated [5] that the content of aromatic compounds for 10 different samples of humic acid averaged  $54.3 \pm 15.2\%$  (compared with  $91.7 \pm 9.9\%$  for the same samples using the oxidation method). Since humic substances appear in all open water sources, their removal is an important task to improve the water quality. Although humic acids represent a diverse and complex range of related compounds, they are not toxic per se, but due to their distinct brownish colour, they make water less attractive to the consumer. Because of the huge volumes involved, effective water purification methods for the removal of humic acids from water supplies have to be efficient, fast and inexpensive. A stirred tank or fluidised bed adsorption setup with dense, high-capacity adsorbent particles would in many situations be preferred to the more costly alternatives, e.g. packed-bed purification systems, because of the scale-up requirements (megalitres per hour requirements are often encountered in water pro-

cess facilities) and the associated process economics. In order to examine these requirements at the laboratory scale, investigations have been carried out with new types of zirconia-based and silica-based adsorbents with surface properties specifically modified to achieve the characteristics of high binding capacity, ease of regeneration and rapid settling rate.

## 2. Experimental

### 2.1. Chemicals

Two types of porous zirconia were used in the investigations. Both types of zirconia particles were synthesised as part of associated projects in this Centre. The first type of zirconia, later referred to as PDZ, was made by using a novel plasma spray process [7], whilst the second type, called M-III, was synthesised by a sol-gel precipitation process. LiChrospher Si-1000 was obtained from E. Merck (Darmstadt, Germany) whilst the Polygosil 300-2540 was obtained from Macherey-Nagel (Düren, Germany). All other

chemicals were purchased from Aldrich (Sydney, Australia) and were at least analytical-grade quality.

## 2.2. Isolation of humic acid from soil

A sample of soil (from the Clayton Campus of Monash University) was washed with water, and 0.01 M HCl. The humic substances, humic and fulvic acids, were extracted with an 0.5 M NaOH solution under exclusion of air. The supernatant of this extraction was acidified to pH 2 with 5 M HCl to precipitate the humic acids, which were recovered by centrifugation and freeze dried. The UV spectrum of this sample showed a shoulder between 250 and 300 nm representing the aromatic components of the humic acids. The absorbance changes at 280 and 254 nm wavelengths of aliquots of the feedstocks containing the recovered humic acids was used to monitor the adsorption of these components to the modified zirconia and silica particles in batch experiments.

## 2.3. Modification of zirconia and silica particles with a hydrophobic quaternary ligand

### 2.3.1. Synthesis of 4-amino-4',4''-bisdimethylaminotriphenylcarbinol (**1**)

The first step in the synthesis of **1** is the condensation of *p*-nitrobenzaldehyde and *N,N'*-dimethylaniline and was based on the procedure by Fischer and Fischer [8–10] (see Fig. 2). *p*-Nitrobenzaldehyde (1.51 g) and *N,N'*-dimethylaniline (2.42 g) were mixed and ZnCl<sub>2</sub> (0.5 g) added. The mixture was heated on a water bath at 100°C. During the condensation reaction, the product developed a green-yellow colour and a resin-like consistency. The product was extracted repeatedly with hot water, then with 0.01 M HCl and finally with diluted ethanol (about 50%, v/v). The resulting yellow crystalline product was then recrystallised from hot toluene. The compound, 4-nitro-4',4''-bis-dimethylanilinomethane (**2**), was slightly soluble in ethanol, insoluble in water, but dissolved easily in 0.01 M HCl forming a colourless solution. The *p*-nitro

compound (**2**) was dissolved in 0.01 M HCl and zinc powder (1 g per g of **2**) added. The suspension was stirred for 2 h at room temperature. The aminocarbinol product (**1**) was precipitated with 1 M ammonium hydroxide as colourless crystals. The precipitate was filtered and recrystallised from benzene or toluene.

### 2.3.2. Modification of the zirconia and silica particles

The aminocarbinol product (**1**) was used as a ligand for modification of the zirconia and silica particles. A hydrothermal treatment was applied to the zirconia and silica particles to ensure a high and uniform hydroxyl group distribution on the zirconia or silica surface. For this purpose, the zirconia (or silica) particles were treated with steam in an autoclave at 150°C for 6 h. Both types of particles were then dried at 180°C under reduced pressure (ca. 0.01 mmHg; 1 mmHg = 133.322 Pa) overnight. Toluene was dried with sodium metal and distilled prior to use. The zirconia (or silica) particles (5 g) were suspended in the distilled, anhydrous toluene (100 ml), 3-isothiocyanatopropyltriethoxysilane (105 mg) (ITCPS) and a catalytic amount of imidazole was added and the suspension stirred under reflux for 24 h. The amount of ITCPS was calculated on the basis of the surface area of the particles, assuming a maximum possible ligand density of about 4 μmol/m<sup>2</sup> and using a two-fold molar excess. To avoid grinding the particles, an overhead stirrer, rather than a magnetic stirrer, was used. The aminocarbinol dye (**2**) was attached to the derivatised zirconia (or silica) particles via the immobilised isothiocyanate (NCS) groups. The aminocarbinol (**2**) (30 mg/g of particles) was dissolved in 50 ml sodium carbonate buffer, pH 7.0, the NCS-derivatised zirconia (or silica) particles added and the suspension stirred at room temperature for 24 h. An *n*-butylamine solution (0.1 M adjusted to pH 7.0) was used to derivatise the remaining NCS groups with the blocking reaction allowed to proceed for 24 h. After the reaction was completed, the particles were washed with 2-propanol, water and hydrochloric acid, pH 3.0, and dried.

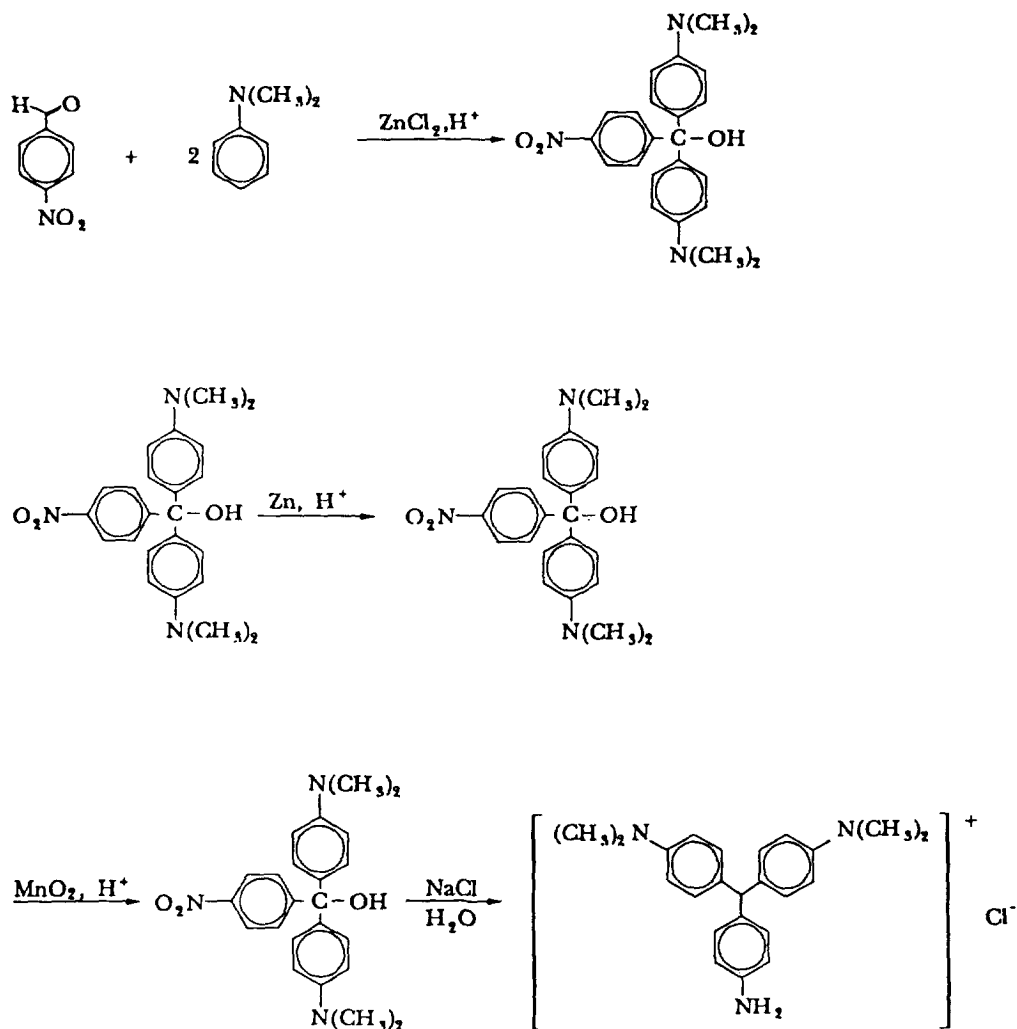


Fig. 2. Synthetic route to the surface modification of the zirconia or silica particles with 4-amino-4',4''-bisdimethylamino-triphenylcarbinol.

#### 2.4. Synthesis of polystyrene with a narrow molecular mass range by anionic polymerisation

Fig. 3 shows the synthetic route for the surface modification of the zirconia and silica particles with polystyrene-based anion exchangers.

##### 2.4.1. Preparation of the initiator

Tetrahydrofuran (THF) was dried over sodium wire overnight. A small amount of benzophenone was added to indicate the water content. Naphthalene (7 g) and sodium metal (1 g)

were added to freshly distilled THF (160 ml). The mixture was stirred under a nitrogen atmosphere for 2 h, developing a dark green colour.

##### 2.4.2. Polymerisation

Dry THF (100 ml) was placed into a 3-neck flask and the initiator solution added dropwise until the green colour remained, indicating that the residual traces of water had been removed. Another 45 ml of the initiator solution were then added. A mixture of styrene (100 ml) in THF

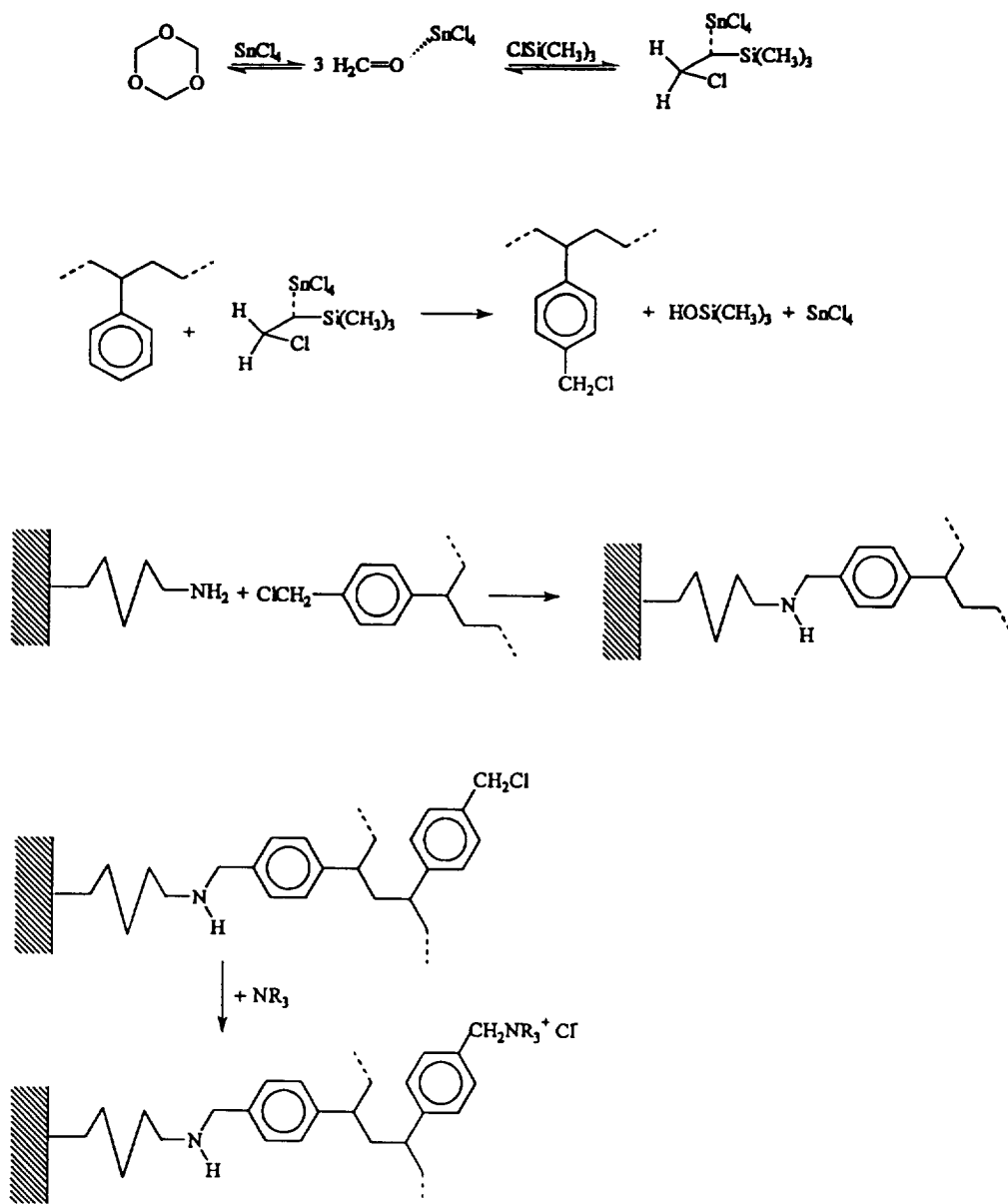


Fig. 3. Synthetic route for the surface modification of the zirconia or silica particles with polystyrene-based anion exchanger.

(300 ml) was added over 30 min. During the polymerisation procedure the solution was stirred vigorously to achieve a uniform growth of all polystyrene molecules. During the addition of the styrene, the solution turned orange-red. The polymerisation was quenched by the addition of methanol to the reaction mixture. The polymer precipitated during the addition of the methanol.

#### 2.4.3. Chloromethylation of polystyrene

Trioxane (0.9 g, 10 mmol), trimethylchlorosilane (3.8 ml, 30 mmol) and polystyrene (1 g) were dissolved in dry chloroform (30 ml) and  $\text{SnCl}_4$  (0.5 ml, 4.3 mmol) added dropwise. The solution was first stirred at  $0^\circ\text{C}$  for 30 min and then at room temperature for 2 h. During the reaction, the colour of the solution turned red.

#### 2.4.4. Modification of zirconia and silica

Zirconia (or silica) (1 g) was activated with 3-aminopropyltriethoxysilane (10 mg) in dry toluene (30 ml) under reflux overnight. The addition of a basic catalyst was not necessary, due to the basic nature of the silane (auto-catalysis). The amino-activated zirconia (or silica) particles (1 g) were suspended in dry dimethylformamide (DMF) (30 ml), an excess of the chloromethylated polystyrene (100 mg) added and the modification reaction carried out under reflux overnight. The coated particles were extensively washed with DMF and toluene to remove any remaining unreacted polystyrene.

#### 2.4.5. Generation of anionic exchange groups

The remaining chloromethyl groups on the immobilised polystyrene were derivatised with trimethylamine or triethylamine. The coated particles were suspended in DMF (1 g in 30 ml) and an excess amount of trimethylamine or triethylamine added. Trimethylamine is a gas at room temperature and condenses at 2.9°C. The free base was liberated from the corresponding hydrochloride with sodium hydroxide and trapped in a dry ice–methanol cool trap. The liquified trimethylamine was transferred into a cooled suspension of the coated particles within an autoclave. In analogous experiments triethylamine was added directly to a suspension of the particles. The reaction was allowed to proceed for 24 h at room temperature.

#### 2.5. Characterisation of the modified zirconia and silica particles in batch experiments

The experimental setup used in this laboratory to characterise the adsorption behaviour of proteins with surface-modified particles has been previously described in detail [11] and consisted of a thermostatted vessel with an inbuilt 1.5- $\mu\text{m}$  frit and an overhead stirrer. A peristaltic pump (Istmatec SA MS Reglo) was used to continuously recycle samples and pump them through a UV monitor (Bio-Rad Ecuno UV). The data were collected with a Datataker 500 data logging device (Data Electronics Australia) and processed on a IBM-compatible personal computer.

### 3. Results and discussion

Humic acids are a complex family of lignin-derived metabolites which contain carboxylic groups with a range of  $pK_a$  values and structural features which involve different types of hydrogen bonding and hydrophobic characteristics. Because humic acid compounds have a high aromatic ring content, we rationalised that these compounds could form  $\pi \rightarrow \pi$  interactions with non-polar aromatic ligands, containing electrostatic groups, immobilised onto a suitable support material. To achieve the required specifications for adsorption with the humic acid class of compounds, a strong quaternary anion exchanger with a significant hydrophobic character due to the presence of substituted phenyl rings was thus selected for these investigations, namely a ligand of the class of the rosaniline dyes. This group of compounds was extensively investigated as dye substances and selected examples synthesised by Fischer and Fischer [8–10] in the second half of the last century. The compound used for the modification in the present investigation was 4-amino-4',4''-bisdimethylaminotriphenylcarbinol (**1**), which is the 4-amino derivative of malachite green. The immobilised aminocarbinol (**1**) exhibits several interesting features with regard to its properties as an anion exchanger. Firstly, under neutral or weakly acidic conditions the immobilised aminocarbinol **1** readily forms a  $\pi$ -bond delocalised carbonium ion and, as such, this compound and its analogues can act [12] as C-type rather than N-type ion exchangers. In addition, these mesomeric compounds undergo dramatic changes in colour when in the hydroxy or in the carbonium ion form. This aminocarbinol derivative of malachite green was synthesised by a two-step procedure. In the first step, *p*-nitrobenzaldehyde was condensed with *N,N'*-dimethylaniline to yield 4-*p*-nitro-*N,N''*-bisdimethylanilinomethane (**2**). In the second step the *p*-nitro compound (**2**) was reduced to the *p*-amino compound with zinc powder under acidic conditions. The reduction reaction first converts the nitro group to an amino group and then reduces the carbinol group. The latter step is not required but since it

is impossible to stop the reaction exactly at the right time, the reduction was allowed to proceed to completion and the hydroxyl group was subsequently reintroduced. The reduced form of the product (**1**) can be oxidised with manganese oxide (1 g per g of **1**) under acidic 0.01 M HCl conditions. A purple dye compound, which can be precipitated with ca. 6 M NaCl was obtained. Under acidic conditions, a proton can be added to the hydroxyl group of the aminocarbonyl dye (**1**) and a water molecule eliminated from the compound. Due to the high mesomeric effect of  $\pi$ -electrons of the phenyl ring systems and the free electron pairs of the amino groups used to immobilise the compound to the support material, the immobilised aminocarbonyl salt is very stable, with the positive charge virtually distributed over the whole molecule. The formation of this salt occurs so readily that it can be achieved by the addition of sodium chloride to a solution of **1**. Furthermore, the extended aromatic ring structure provides a hydrophobic characteristic with the hydrophilic influence of the amino groups shielded by the methyl groups. The dye (**1**) was attached to ITCPS-modified support materials, exploiting an immobilisation procedure which we have extensively utilised on previous occasions. The attachment group adds to the mesomeric stabilisation of the charged aminocarbonyl compound. The remaining unreacted NCS groups were derivatised with *n*-butylamine to further enhance the hydrophobicity of the chemically modified zirconia (or silica) surface. The hydrophobicity of the final adsorbent can thus be adjusted by the type of *n*-alkylamine used to derivatise the remaining NCS groups [13]. Suitable alkylamines range [13] from *n*-octadecylamine as a more hydrophobic *n*-alkylamine to ethanolamine as a more hydrophilic *n*-alkylamine.

For the preparation of the strong anionic exchangers, the zirconia (or silica) particles were modified with a polystyrene-based coating [14–17]. Again, the approach to the development of these ion-exchange adsorbents suitable for humic acid substances was predicated on the presence of an aromatic ring structure as part of the ligand composition. The zirconia particles were hydro-

thermally treated as described above and modified with 3-aminopropyltriethoxysilane [18]. Styrene was polymerised using the anionic polymerisation procedure with sodium naphthalene used as the initiator to achieve a narrow molecular mass range [19]. The polymer was chloromethylated [20] and coupled to the amino-modified zirconia (or silica). An excess amount of chloromethylated polystyrene was added to the suspension of the surface-activated zirconia (or silica) ensuring that only a small portion of the chloromethyl groups of a given polystyrene chain had the chance to react with the activated zirconia (or silica), leaving the majority of the chloromethyl groups unmodified. This protocol resulted in a high amount of chloromethyl groups available for the generation of ion-exchange groups as well as resulting in a “tentacle-type” modification. The unreacted chloromethyl groups were derivatised with either trimethylamine or triethylamine resulting in a zirconia (or silica) adsorbent chemically coated with polystyrene-trimethylammonium chloride or polystyrene-triethylammonium chloride groups.

With complex mixtures of compounds that have very similar structural and detection features, the determination of the adsorption isotherms of an individual compound can present a significant experimental challenge. This situation is particularly the case with complex mixtures derived from humic acid compounds where the concentration of individual components may be very low yet the overall concentration of related isomeric components or their derivatives can be relatively high [5]. In these circumstances, the adsorption behaviour of these similar compounds can be characterised in terms of their apparent adsorption isotherms provided several assumptions are tenable. In particular, the relative affinities of the related components for the adsorbent should be similar, the components should bind to the ligands by similar mechanisms and their molar concentrations should fall within a range where displacement and band distortion phenomena do not significantly perturb the isothermal behaviour. Under such conditions, experimental derivation of the apparent overall adsorption isotherms with different adsorbents

can be achieved but it should be noted that these profiles will reflect only the average behaviour of these related compounds within the mixture rather than the isothermal behaviour of an individual member. These apparent (or average) adsorption isotherms for the humic acid preparation with the aminocarbinol-modified adsorbents were determined using the temperature-controlled recycling bath system essentially as described in our earlier publication [11]. In brief, the aminocarbinol-modified adsorbent was suspended in water (1 g adsorbent per 25 ml) and aliquots of a solution of the humic acid preparation (1 mg/ml) were added. The adsorption of the humic acid components at 25°C was continuously monitored at 280 nm utilising the detector which forms part of the recycling system. The adsorption data derived from the change in optical density of the recycle as a function of time and concentration were then evaluated in terms of a single-component Langmuirean ad-

sorption model [21] which takes into account the assumptions itemised above. From these data, it is also possible to calculate a value of the apparent (or average) maximum capacity by using different linearisation procedures developed by Benesi and Hildebrand [22], Scatchard [23] and Scott [24]. The derived plots, corresponding to the apparent adsorption isotherms for the aminocarbinol-modified Polygosil 300-2540 with this humic acid preparation as well as the linearisation plots shown in Fig. 4 are representative of the experimental results obtained with the other different adsorbents. As evident from Fig. 4, good agreement existed between the linearisation of these experimental data and the theoretical predictions of the Langmuirean model. Because of the structural complexity of the humic acid sample, a value for the association constant cannot however be derived whilst the maximum capacity ( $q_m$ ) can only be expressed in terms of mg/g. The apparent  $q_m$

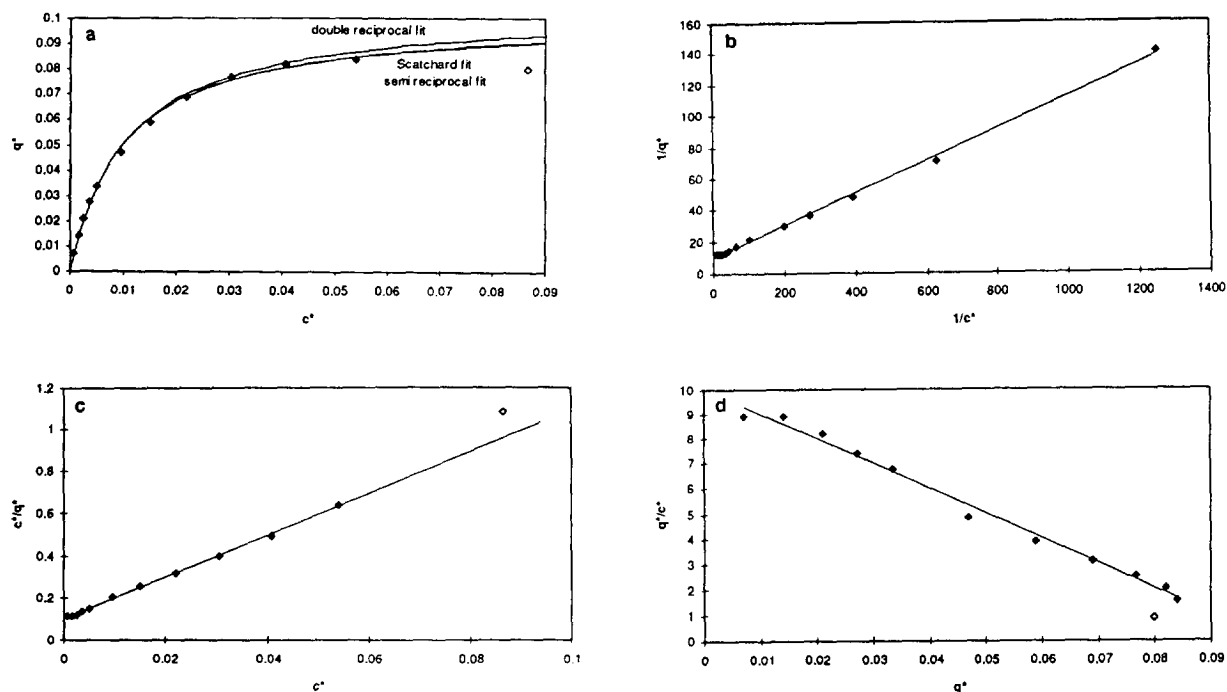


Fig. 4. Adsorption isotherms of the humic acid sample in the Barossa Valley water measured with the aminocarbinol modified Polygosil (300-2540) silica anion-exchange adsorbent. The  $c^*$  represents the free humic acid concentration in the supernatant while  $q^*$  represents the amount of adsorbed humic acid. (a) Semi-reciprocal plot (Scott plot); (b) Scatchard plot; (c) adsorption isotherm; (d) double reciprocal plot (Benesi-Hildebrand plot).



value was about 90 mg humic acid per g silica for this aminocarbonyl modified Polygosil 300-2540 adsorbent.

To determine the effectiveness of the humic acid removal from a river water sample obtained from a wine growing district in South Australia, different amounts of the modified zirconia and modified silica adsorbents were suspended in 50 ml of the water sample under controlled-temperature conditions and the adsorption process monitored continuously from the change in optical absorbance at 254 nm. The adsorption curves for these different adsorbents are shown in Figs. 5–8. Representative of the effectiveness of the regeneration procedure are the results shown in Fig. 8 for the triethylphenylammonium polystyrene-coated zirconia M-III when incubated with the Barossa Valley water (1 g adsorbent per 100 ml water) for 30 min, and the adsorbent then regenerated with a concentrated NaCl solution (brine) (1 g adsorbent per 100 ml brine). This adsorption/desorption cycle was repeated four times. These conditions were chosen to enable regeneration of the modified particles to occur as rapidly and as completely as possible. Consequently, this process has not been optimised in terms of brine usage nor have multiple small-step elution washes rather than a single-step batch elution been examined at this stage as alternative regeneration protocols. As evident from these data on the repetitive adsorption/regeneration measurements with the triethylphenylammonium

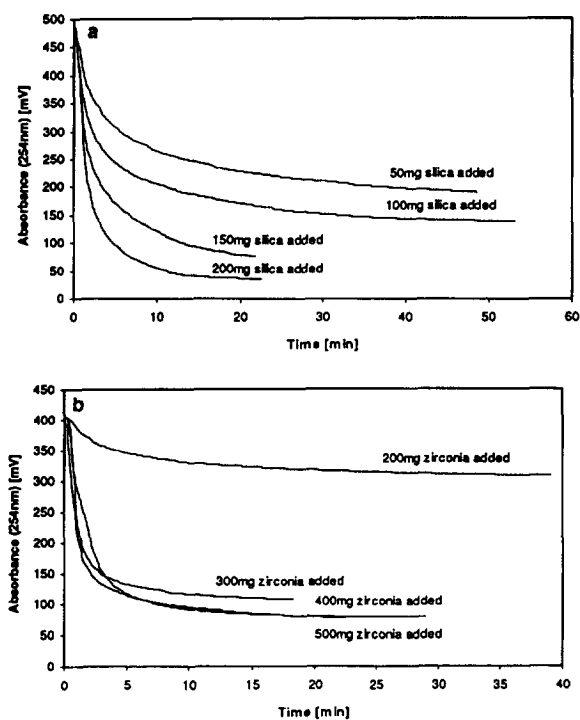


Fig. 6. (a) Adsorption curves of the humic acid sample in the Barossa Valley water with triethylphenylammonium SAX-modified LiChrospher Si-1000 adsorbent. (b) Adsorption curves of the humic acid sample in the Barossa Valley water with triethylphenylammonium SAX-modified zirconia M-III adsorbent.

strong anion-exchange (SAX)-modified M-III zirconia, there is discrete difference between the first and the following loadings which might be

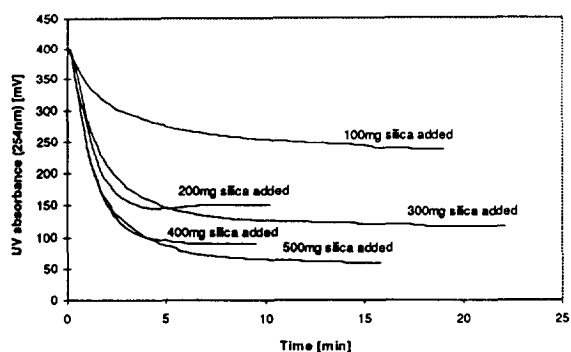


Fig. 5. Adsorption curves for the humic acid sample in the Barossa Valley water with the aminocarbonyl-modified LiChrospher Si-1000 adsorbent.

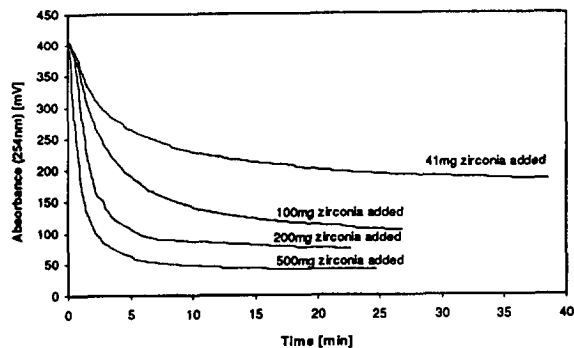


Fig. 7. Adsorption curves of the humic acid sample in the Barossa Valley water with trimethylphenylammonium SAX-modified PDZ adsorbent.

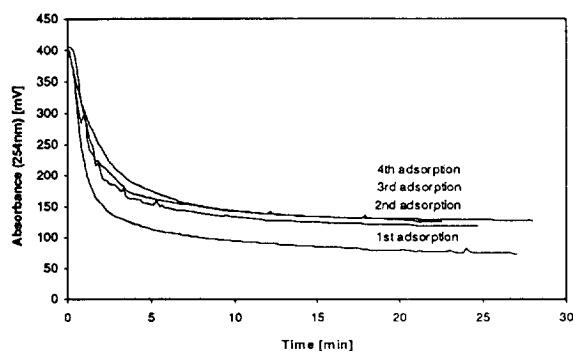


Fig. 8. Repetitive adsorption and elution measurements with the triethylphenylammonium SAX-modified M-III zirconia and the Barossa Valley water.

due to irreversible adsorption of humic acid components onto unmodified regions of the zirconia surface or due to strong non-ionic interactions (e.g. hydrophobic interactions) between the solutes and the polymeric coating. After the first cycle, the adsorbent can be reproducibly regenerated. As can be seen from the results summarised in Figs. 4–8, the success of removing the humic substances, which adsorb in the UV at 254 nm, from the water sample is dependent on the electrostatic/hydrophobic balance of the ion-exchange adsorbent and the type of support material. The similarity of the adsorption behaviour when using 800 mg or 1 g of the triethylphenylammonium SAX-modified Li-Chrospher Si-1000 per 100 ml water, shown in Figs. 5 and 6b, and the relatively small difference when using 400 mg and 1 g of the triethylphenylammonium SAX-modified zirconia M-III per 100 ml shown in Fig. 8 indicates that the remaining components in the water sample represent substances which cannot be removed by an ion-exchange process.

It can be concluded from the above results that the humic acid substances in Barossa Valley water consist of a variety of compounds with different affinities for the prepared ion exchangers. The three different surface-modification procedures resulted in adsorbents which exhibit different ion-exchange characteristics, binding affinities and capacities. The aminocarbinol modification leads to relatively weak

anion exchangers, whilst the triethyl- and trimethylphenylammonium chloride modifications generated strong ion exchangers. As evident from these results the trimethylphenylammonium modification resulted in an even stronger ion exchanger than the triethylphenylammonium modification. The various strengths of the ion exchangers dominate the way the adsorbents interact with the humic substances in the water. Besides affecting the maximum value of the apparent adsorption capacity, the density and chemical characteristics of the ligand also affect the adsorption kinetics. From the data obtained with the kinetic measurements of the change in optical density as a function of adsorption time, the best performances were observed when the aminocarbinol- and the trimethylphenylammonium SAX modifications were used, whilst the triethylphenylammonium modified SAX particles showed a significantly slower rate of adsorption.

In conclusion, the results achieved from these laboratory-scale experiments in terms of the apparent adsorption capacities and binding behaviour with the surface-modified porous zirconia were comparable to the results achieved with porous silica. Due to the higher density of zirconia, however, these particles should exhibit a distinct advantage in terms of their settling rate when they are employed at a larger scale in batch or expanded bed processes. Faster settling rates mean that faster separation times between the liquid and the solid phase can be achieved resulting in an increase in efficiency due to a reduced cycle time. An important advantage of the surface-modified zirconia adsorbents relate [7] to their high chemical stability over a wide range of pH conditions, thus offering a greater variety of elution and regeneration possibilities.

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