



## HUMIC SUBSTANCE UPTAKE BY HYDROTALCITES AND PILCS

S. AMIN\* and G. G. JAYSON

School of Chemical and Physical Sciences, Liverpool John Moores University, Liverpool L3 3AF, England

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**Abstract**—Pollution of natural waters is usually concerned with the presence of undesirable toxic substances and heavy metals resulting from man made sources. However, there are already considerable concentrations of undesirable species in natural systems such as humic substances and heavy metals that occur in upland surface water. Synthetic hydrotalcite clays were found to be very effective in removing humic substances from upland surface water due to their anionic nature. Pillared interlayer clays (PILC's) removed humic substances, but to a much lesser extent and this was related to their cationic nature and to the interlayer spacing. Uptake of humic substances from upland surface water was more effective at lower pH values.

**Key words**—hydrotalcites, pillared clays, PILC, humic substances, adsorption

### INTRODUCTION

Activated carbon in the granular form is the principal adsorbent being used to remove organic compounds from drinking water. Humic substances constitute a major fraction of organic matter in natural water and effluents and their presence has been a problem facing the water industry. The yellow to brown colour of these waters is mainly due to the presence of aquatic humic and fulvic acids (Zhou and Banks, 1992, 1993). Some of the most important characteristics exhibited by all humic fractions is their resistance to microbial degradation, and the ability to form stable water soluble and insoluble salts and complexes with metal ions and hydrous oxides and to interact with clay minerals and organic chemicals (Schnitzer and Khan, 1972). Therefore, the reaction of humic substances in upland surface water with clay minerals should be of considerable interest to those concerned with environmental problems.

There are many other insoluble materials other than activated carbon, that have the potential for removing humic substances from water such as natural and synthetic zeolites, clays and modified clay minerals, aluminas and resins. This study was designed to assess the effectiveness of anionic hydrotalcite clays and cationic clay minerals in the removal of humic substances from upland surface water. It was proposed to take advantage of the anionic exchange capability of the hydrotalcite clays to remove humic

substances. For the modified cationic clays, it was proposed to take advantage of the interlayer spacing in the clays as well as surface adsorption processes.

### MATERIALS AND METHODS

#### *Preparation of hydrotalcites*

Various methods were used for the synthesis of the hydrotalcites. The carbonate form of hydrotalcite was prepared following a method described by Reichle (1985). A solution of 1.0 M  $\text{Mg}(\text{NO}_3)_2/0.5 \text{ M Al}(\text{NO}_3)_3$  was made by dissolving  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (25.6 g) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (18.75 g) in distilled water (100 ml). The above solution was added dropwise to a solution of 50% aqueous NaOH (28 g) and  $\text{Na}_2\text{CO}_3$  (10 g) in distilled water (100 ml), in a 1 litre four necked round bottomed flask immersed in a cooling bath, and equipped with a mechanical overhead stirrer, reflux condenser, thermometer and dropping funnel. The addition was carried out over 30 min keeping the temperature below 308 K. Following addition, the slurry was heated to 338 K for 18 h with stirring. The slurry was then allowed to cool, filtered and washed with de-ionised water. The sample ( $\text{HTCO}_3$ ) was dried at 398 K for 18 h in a vacuum oven.

The nitrate form of hydrotalcite was prepared by dissolving  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (72.56 g) in distilled water (250 ml).  $\text{MgO}$  (23.4 g) was then suspended in distilled water (125 ml). The two solutions were then thoroughly mixed using an overhead stirrer. The resulting mixture was put into a polypropylene bottle, sealed and placed in the oven at 363 K for 6 days. The sample ( $\text{HTNO}_3$ ) was then filtered and washed with de-ionised water and the solid oven dried at 363 K.

A third method was used to prepare the carbonate and nitrate forms of hydrotalcite. The carbonate form ( $\text{HTC}$ ) was prepared by dissolving NaOH (37.5 g) and  $\text{Na}_2\text{CO}_3$  (33 g) in de-ionised water (1000 ml). The metal salt solution was prepared by dissolving  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (46.5 g) and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (96 g) in de-ionised water (187.5 ml), and then this slowly added to the alkali solution and the resulting mixture stirred under constant reflux at 368 K for

\*Author to whom all correspondence should be addressed, at: BNFL plc, Sellafield R&D, Seascale, Cumbria CA20 1PG, England [Tel.: (44) 19467 74598; Fax: (44) 19467 75698].

2 h using an overhead stirrer in order to effect hydrothermal ageing. The slurry was then filtered and washed with de-ionised water and oven dried at 368 K. The nitrate form (HTN) was prepared in the same manner, except that no  $\text{Na}_2\text{CO}_3$  was added.

#### *Preparation of pillared clays (PILCS)*

**Method 1.** Zirconium pillared clays were prepared following the method described by Dyer (1989), and Velazquez (1990). Montmorillonite, bentonite and kaolin clay samples were used for the preparation of the PILCS and were used "as received". To each clay sample (20 g), fresh 0.10 M zirconyl chloride solution (600 ml) was added. The slurry was then stirred for 24 h, filtered and washed free of chloride with de-ionised water and tested with 0.10 M  $\text{AgNO}_3$ . The montmorillonite, kaolin and bentonite PILCS (MZRT, KZ and BZ respectively) were oven dried at 378 K.

**Method 2.** Montmorillonite clay (20 g) was added to 0.10 M zirconyl chloride solution (600 ml) which had been previously refluxed for 24 h. The resultant slurry was then treated as above to obtain the PILC (MZR).

**Method 3.** As method 2 but the resulting slurry was then refluxed at a constant 363 K for a further 2 h, and then the resulting mixture treated as above to obtain the PILC (MRZR).

#### *Removal of humic substances from upland surface water*

The above prepared hydrotalcite and PILC samples were used to investigate the removal of humic substances from upland surface water supplied by North West Water from Laneshaw Reservoir, Laneshaw Bridge, Nr. Colne, East Lancs.

Clay samples (0.5 g) were accurately weighed into 25 ml screw top bottles and upland surface water added (20 ml). Liquid:solid ratio was 40:1. The pH of the resulting slurry was measured. The bottles were then sealed and placed on a mineral roller for a period of 1, 3, 5, 7, and 14 days after which time samples were removed and the pH of the slurry measured again. Samples were then filtered to dryness under vacuum and the filtrate collected.

In addition, the total uptake capacity of the clays for humic substances was investigated. This was done by placing the clay samples (0.10 g) in contact with a 500 mg/l humic acid solution (50 ml). The sample bottles were then placed on a mineral roller and agitated for a period of 2 weeks after which time the samples were removed and filtered to dryness under vacuum and the filtrate collected.

#### *Effect of pH on the removal of humic substances from upland surface water*

Clay samples (0.2 g) were accurately weighed into 25 ml screw top bottles and upland surface water added (20 ml). Liquid:solid ratio was 100:1. The pH of the resulting slurry was measured and then adjusted to pH 3 and pH 5 for each clay sample using 0.10 M HCl and 0.10 M NaOH solutions. Samples were placed on a mineral roller for 1 and 7 days after which time samples were removed and the pH of the slurry measured again. Samples were then filtered to dryness under vacuum and the filtrate collected.

#### *Characterisation of samples*

The u.v. absorption analysis of the upland surface water and filtrates was carried out on a Hewlett Packard 8452A Diode Array Spectrophotometer. All analyses were performed at 254 nm using a 1 cm quartz cell. Standard humic acid solutions were prepared by dissolving the sodium salt of humic acid (Aldrich Chemicals) in de-ionised water to make a 1000 mg/l solution. This stock solution was diluted to prepare a series of standard solutions.

Differential thermogravimetric analysis was performed on a Mettler TG50 system. Samples to be analysed were first placed in a vacuum desiccator and allowed to equilibrate over a saturated NaCl solution for at least 1 week. The

equilibrium water content of the samples was determined by heating the samples to 973 K using a heating rate of 20 K/min.

X-ray diffraction analysis of the clay samples was carried out on a Philips 1710 diffractometer using  $\text{CuK}\alpha$  radiation. X-ray fluorescence analysis was carried out on a Philips PV9550 system.

A Dionex DX-100 Ion Chromatograph System equipped with an Ion-Pac AS4A-SC separator column and an Ion-Pac AG4A-SC guard column, was used for the analysis of anions collected in the filtrate samples. The system was calibrated using 4, 6, 8, 10, 20 and 30 ppm standard solutions of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ . All samples were filtered on Whatman GF/F glass filter paper prior to injection.

## RESULTS

### *U.V. absorbance of humic substances in the filtrates*

The humic content of the upland surface water was found to be 12.28 mg/l, as measured by u.v. absorbance at 254 nm. Initial experiments found that the absorbance of the filtrates was not only due to the presence of humic substances, but also to the possible dissolution of the clay samples in contact with the upland surface water. Therefore, clay + de-ionised water samples were used as the blank for each respective clay in the u.v. absorbance measurements. Results are given in Figs 1–4. Table 1 gives the uptake capacity of the clays, for humic substances.

### *Ion chromatography*

A sample of filtered upland surface water was analysed and the results are given in Table 2. In order to see whether or not any leaching of anions from the clays occurred, samples of the clay + de-ionised water were used as controls. Samples were analysed after several days of agitation on the mineral roller and the results given in Tables 3–4.

### *pH Measurements*

The pH of the upland surface water as well as the clay slurries was measured and the results given in Tables 5–6. The pH of the upland surface water was 6.49.

### *X-Ray diffraction and X-ray fluorescence*

X-Ray diffraction was used to determine the crystallinity and also the interlayer *d*-spacing of the samples. Particle size of the clays was calculated from the XRD data using Philips PC-APD software and a potassium chloride standard, whilst X-ray fluorescence was used to determine the amount of zirconium in the natural clays after the pillaring process. The results are given in Table 7.

### *Thermal analysis*

Thermal analysis of the clay samples before and after treatment with upland surface water were carried out and the results given in Table 8.

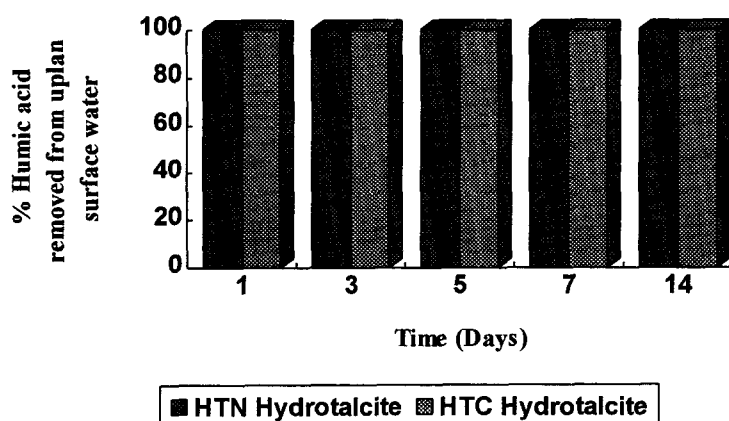


Fig. 1. Uptake of humic acid from upland surface water by hydrotalcite clays.

### DISCUSSION

#### *X-Ray diffraction and X-ray fluorescence*

The X-ray diffractograms of the anionic hydrotalcite clays all indicated fairly good crystallinity, and all samples were identified as hydrotalcite phases. However, definite variations in the degree of crystallinity were observed for the nitrate and carbonate forms of the hydrotalcite. This variation seems to result from the method of synthesis employed. For the HTNO<sub>3</sub> sample, maximum crystallinity was not achieved and this was probably related to the time allowed for ageing of the sample. The HTCO<sub>3</sub> sample showed excellent crystallinity, with no broad peaks in the XRD diffractogram after an ageing time of 18 h. The HTN and HTC samples both showed fairly good crystallinity even after only 2 h hydrothermal ageing. Therefore, ageing appears to be one of the most important factors controlling crystallinity of the samples and this in turn will affect the *d*-spacings. The values of *d*-spacing obtained for the HTN and HTC samples were 8.73 and 7.75 Å respectively. This

was as expected since the nitrate ion is larger than the carbonate ion and the *d*-spacing values obtained for the samples agree very well with those in literature (Miyata, 1983).

The most noticeable feature of the XRD diffractograms of the natural clays and their derivative PILCS was that there was a shift of the *d*(001) peak to lower  $2\theta$  values, for the PILCS, corresponding to the expansion of the interlayer spacing due to pillaring by zirconium. The pillaring process causes an increase in the interlayer spacing and this was confirmed by XRD analysis. The *d*-spacing of the parent montmorillonite clay increased from 14.56 to 15.55 Å and 16.76 Å for the MZRT and MZR PILCS respectively (Table 6). The MRZR PILC only showed a *d*-spacing of 9.94 Å indicating a reduction in the interlayer spacing. The parent bentonite sample had a *d*-spacing of 15.10 Å which increased to 17.03 Å upon pillaring with zirconium. The kaolin PILC showed only a modest *d*-spacing of 10.18 Å.

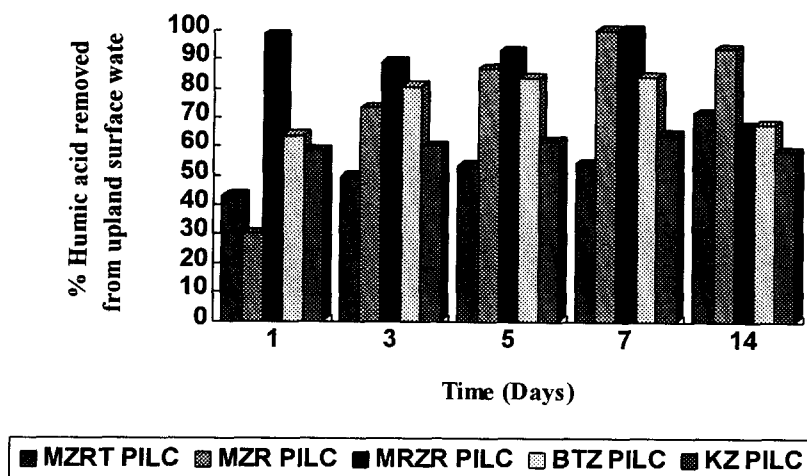


Fig. 2. Uptake of humic acid from upland surface water by PILCS.

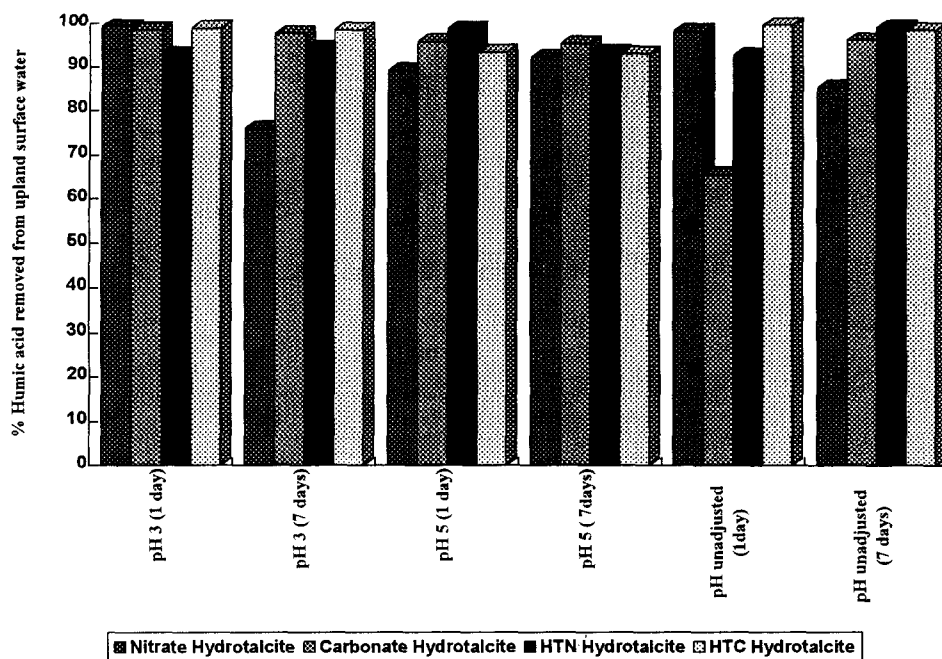


Fig. 3. Uptake of humic acid from upland surface water by hydrotalcite clays—pH adjusted.

Results given in Table 7 indicate fairly large particle sizes, as calculated from the XRD data. This is probably due to the clays occurring as an aggregate of small crystallised particles. Crystallite sizes of hydrotalcites are very dependent upon method of synthesis and treatment. According to X-ray diffraction analysis (Miyata, 1975), hydrotalcite samples consist of spherical aggregates (about 10–50  $\mu\text{m}$ ) which are formed by strong coagulation of microcrystals

(order of magnitude: 100  $\text{\AA}$ ). Larger crystallites of hydrotalcite have been noted (Miyata *et al.*, 1977) and larger crystals can be prepared, depending upon the method of synthesis as particles aggregate to form secondary units or tertiary units. Hydrothermal treatment of hydrotalcites can increase the crystallite size considerably (Miyata, 1980).

X-ray fluorescence in conjunction with XRD analysis was useful in showing the effectiveness of the

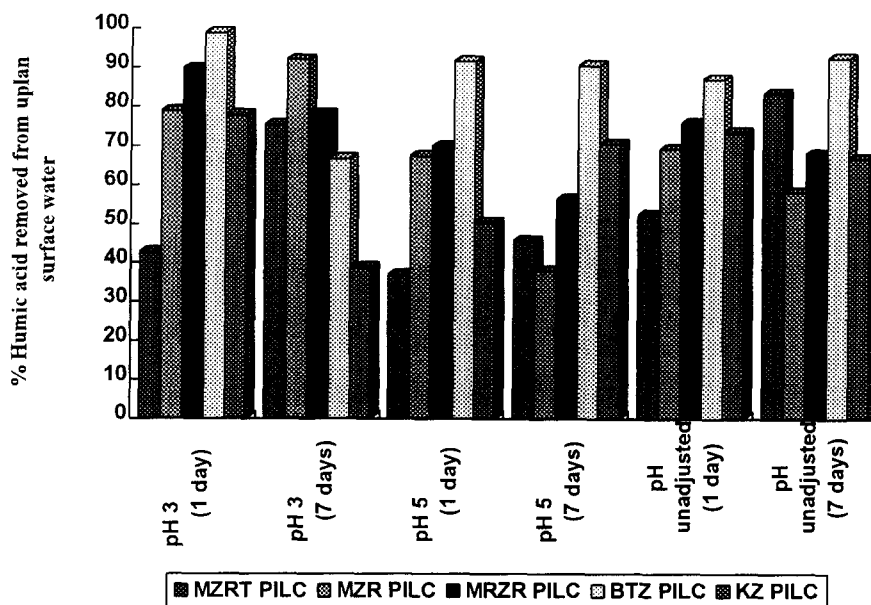


Fig. 4. Uptake of humic acid from upland surface water using PILCS—pH adjusted.

Table 1. Humic uptake capacity of the clays

Clay sample	g of Humic substance per g of clay
Hydrotalcite (HTNO <sub>3</sub> )	1.79
Hydrotalcite (HTCO <sub>3</sub> )	1.86
Hydrotalcite (HTN)	1.97
Hydrotalcite (HTC)	1.90
Montmorillonite PILC (MZRT)	1.14
Montmorillonite PILC (MZR)	1.35
Montmorillonite PILC (MRZR)	1.38
Bentonite PILC (BTZ)	0.65
Kaolin PILC (KZ)	1.04

Table 2. Ion concentration in the upland surface water

Average Cl <sup>-</sup> (ppm)	Average NO <sub>3</sub> <sup>-</sup> (ppm)	Average SO <sub>4</sub> <sup>2-</sup> (ppm)
11	2	13

pillaring process. Successive degrees of treatment of the zirconyl chloride resulted in an increase in the amount of zirconium in the pillared clay and this can be related to the *d*-spacings obtained for the respective clays. The MRZR PILC showed a large percentage of Zr in the sample by XRF analysis, but XRD results showed that the *d*-spacing had been reduced. Two possible explanations exist for this. Firstly, the zirconium has not been effective in pillaring the montmorillonite clay. The second explanation is that the *d*-spacing is quite large and that the XRD analysis needs to be carried out at lower  $2\theta$  values.

#### Thermal analysis

Differential thermogravimetric analysis (DTG) can provide information on different types of binding of water molecules as well as sitings of water molecules and exchanged or sorbed molecules.

Thermal analysis of hydrotalcites has been fully described elsewhere (Miyata, 1975; Miyata, 1977; Miyata, 1980; Pesic *et al.*, 1992; Reichle *et al.*, 1986; Sato *et al.*, 1986). The general trend is that interstitial water is lost up to 573 K and normally occurs in two stages. Endothermic peaks above 573 K are indicative

of loss of water due to dehydroxylation, as well as carbon dioxide (Miyata, 1977) in the case of the carbonate form of hydrotalcite. On heating above 573 K the interstitial water molecule and decomposition product or products of the anion are expelled and the hydroxyl groups are converted to metal oxide and water. Hydrotalcite samples treated with upland surface water showed a very slight shoulder on the first endothermic peak which could possibly be due to weakly physisorbed or ion-exchanged humic substances coming off during heating.

The DTG's of the PILCS and their starting materials showed very little variation after treatment with upland surface water due to the fact that there was only a small amount of humic substance in the upland surface water. There was in some cases a slight broadening of the peaks or a small shift to higher temperatures. The findings were consistent with those reported in the literature (Schnitzer and Khan, 1972) where the reaction of fulvic acid (humic substance) with natural clays has been studied. It was found that fulvic acid reacts with Na-Montmorillonite by adsorbing on its external surfaces and also by entering into the interlayer spaces.

Ion exchange would not be expected to occur in the PILCS as the exchangeable ions are positive and humic species are negatively charged. Ion exchange would be expected in the hydrotalcites but as with the PILCS, the concentration of humic species in the upland surface water seems sufficiently small so as not to be able to distinguish endothermic peaks due to the presence of adsorbed or ion exchanged humic species; rather the humic substances which are taken up by the hydrotalcites and PILCS, are lost during heating along with loosely held water and interstitial water, so as not to be distinguishable as peaks in their own right.

#### Uptake measurements of humic substances

Absorption in the u.v. region is due to the presence of multiple bonds and unshared electron pairs in

Table 3. Ion concentration for clay + de-ionised water (liquid:solid ratio = 40:1)

Clay + de-ionised water sample	Average Cl <sup>-</sup> (ppm)	Average NO <sub>3</sub> <sup>-</sup> (ppm)	Average SO <sub>4</sub> <sup>2-</sup> (ppm)
Hydrotalcite (HTN)	7	1040	0
Hydrotalcite (HTC)	1	330	0
Montmorillonite PILC (MZRT)	97	1	0
Montmorillonite PILC (MZR)	96	0	0
Montmorillonite PILC (MRZR)	150	1	0
Bentonite PILC (BTZ)	149	1	0
Kaolin PILC (KZ)	22	1	0

Table 4. Ion concentration for clay + de-ionised water (liquid:solid = 100:1)

Clay + de-ionised water sample	Average Cl <sup>-</sup> (ppm)	Average NO <sub>3</sub> <sup>-</sup> (ppm)	Average SO <sub>4</sub> <sup>2-</sup> (ppm)
Hydrotalcite (HTNO <sub>3</sub> )	2	413	0
Hydrotalcite (HTCO <sub>3</sub> )	1	19	0
Hydrotalcite (HTN)	2	628	0
Hydrotalcite (HTC)	3	142	0
Montmorillonite PILC (MZRT)	37	1	0
Montmorillonite PILC (MZR)	46	0	0
Montmorillonite PILC (MRZR)	79	0	0
Bentonite PILC (BTZ)	65	0	0
Kaolin PILC (KZ)	9	0	0

Table 5. pH of clay + upland surface water (liquid:solid ratio = 40:1)

Clay sample	pH of the clay + upland surface water slurry					
	At start	1 day	3 days	5 days	7 days	14 days
HTN	7.50	8.02	8.55	9.04	7.70	8.28
HTC	9.11	8.95	8.53	8.90	9.05	9.09
MZRT	2.35	2.74	3.21	3.02	2.84	3.60
MZR	2.39	2.59	2.49	2.55	2.65	3.65
MRZR	2.25	2.41	3.22	2.29	3.63	2.21
BTZ	2.36	2.50	2.44	2.59	2.58	2.39
KZ	2.93	3.63	4.14	3.76	4.42	3.64

Table 6. pH of clay + upland surface water—pH adjusted samples (liquid:solid ratio = 100:1)

Clay sample	Before pH adjustment	pH of the slurry		After 1 day	After 7 days
		After pH adjustment	After 1 day		
Hydrotalcite (HTNO <sub>3</sub> )	5.69	3	6.76	8.64	
		5	7.19	8.25	
Hydrotalcite (HTCO <sub>3</sub> )	7.89	3	4.24	8.27	
		5	7.67	8.85	
Hydrotalcite (HTN)	5.93	3	6.39	8.74	
		5	8.13	9.10	
Hydrotalcite (HTC)	7.83	3	7.17	8.34	
		5	8.82	9.31	
Montmorillonite PILC (MZRT)	3.31	3	2.92	3.20	
		5	4.60	4.01	
Montmorillonite PILC (MZR)	3.35	3	2.43	3.01	
		5	4.03	3.96	
Montmorillonite PILC (MRZR)	3.02	3	2.95	3.12	
		5	3.56	3.47	
Bentonite PILC (BTZ)	3.23	3	2.46	3.16	
		5	3.89	3.77	
Kaolin PILC (KZ)	5.32	3	2.37	2.87	
		5	4.54	5.07	

organic molecules. Humic substances contain phenolic and various aromatic and possibly aliphatic functional groups, which act as chromophores in the u.v.-vis regions of the electromagnetic spectrum (Greenland and Hayes, 1978). Typical u.v. spectra of most humic substances are featureless, with the optical density decreasing as the wavelength increases (Schnitzer and Khan, 1972).

Figures 1–2 demonstrate the general trends for the uptake of humic substances. Hydrotalcites were extremely effective in removing humic substances at this liquid:solid ratio of 40:1, showing a 100% removal after just 1 day of contact. The montmorillonite PILCS (Fig. 2) demonstrate quite clearly the effect of time of contact with the upland surface water and also the effect of increased pillaring. Sample MZRT clearly showed that with increasing time, more humic acid was removed from the upland surface water and taken up by the clay. Increased pillaring (MZR and MRZR samples) proved that as well as being

adsorbed onto the clay surface, the humic acid must be taken up into the interlayered spaces since the MZR sample showed a 100% uptake of humic acid after just 3 days. Sample MRZR was slightly out of sequence, but this result was consistent with the XRD and XRF findings which showed that the MRZR sample had a much reduced *d*-spacing, whereas the XRF results showed the MRZR sample to have the largest percentage of Zr present after the pillaring process. A possible explanation is that Zr may be deposited on the surface of the montmorillonite as zirconium hydroxide and this may itself be acting as a centre of adsorption, since if the MRZR sample was sufficiently pillared, as in the MZR sample, then the humic acid should have been totally removed from the upland surface water. With the bentonite PILC the uptake process seems to be more time dependent since its *d*-spacing was 17.03 Å, whereas the MZR sample had a *d*-spacing of 16.76 Å. Also the percentage of Zr in these two samples was very similar

Table 7. Interlayer spacing and particle size of the clays and percentage of zirconium in the PILCS

Clay sample	<i>d</i> -Spacing (Å)	Particle size (Å)	% Zirconium in sample after pillaring
Hydrotalcite (HTNO <sub>3</sub> )	7.70	131	—
Hydrotalcite (HTCO <sub>3</sub> )	7.71	427	—
Hydrotalcite (HTN)	8.73	62	—
Hydrotalcite (HTC)	7.75	102	—
Montmorillonite PILC (MZRT)	15.55	962	24.68
Montmorillonite PILC (MZR)	16.76	513	35.70
Montmorillonite PILC (MRZR)	9.94	290	39.99
Bentonite PILC (BTZ)	17.03	1022	32.98
Kaolin PILC (KZ)	10.18	564	6.36

Table 8. Weight loss of clay samples heated up to 973 K

Sample	Weight loss (%) (untreated sample)	Weight loss (%) (treated sample)
Hydrotalcite (HTN)	48.64	56.77
Hydrotalcite (HTC)	47.78	49.18
Montmorillonite PILC (MZRT)	22.88	46.48
Montmorillonite PILC (MZR)	23.08	45.69
Montmorillonite PILC (MRZR)	24.27	40.31
Bentonite PILC (BTZ)	20.75	24.61
Kaolin PILC (KZ)	14.64	21.27

(Table 7). This further substantiates that the uptake of humic acid from upland surface water is not simply controlled by degree of pillaring or the percentage of Zr present in the form of oxide or hydroxide, rather it is a combination of the above factors. The kaolin clay was somewhat of an anomaly, results showing that uptake of humic acid is primarily controlled by interlayer spacing in the case of the kaolin PILC.

The uptake capacity of the clays for humic substances was also investigated, the results given in Table 1 following the previously observed trends. The carbonate and nitrate forms of hydrotalcite showed a considerable uptake capacity for humic substances, and these were significantly higher than the values obtained for the uptake capacity of the PILCS for humic substances. The montmorillonite PILCS showed an increasing uptake capacity for humic substances as the percentage of zirconium present in the montmorillonite samples increased. The bentonite PILC showed a relatively low uptake capacity for humic substances despite its large *d*-spacing and high zirconium content (Table 7). The kaolin PILC also gave a relatively low uptake capacity for humic substances. It would therefore appear that uptake of humic substances by the PILCS is controlled by a variety of factors, as mentioned earlier, including the framework structure.

#### *Effect of pH*

For the hydrotalcites, it was noted that the initial starting pH of the slurry was relatively high and continued to rise slowly. The PILCS were much more acidic in nature, the greater the amount of zirconium in the sample, then the lower the pH of the slurry. The effect of adjusting the pH of the slurry (Table 6) shows that the pH eventually starts to equilibrate out over time. However, Figs 3–4 indicate that the pH of the slurry directly affects the uptake and adsorption of humic acid from upland surface water. For the hydrotalcites, there doesn't appear to be much difference in the humic acid uptake. The montmorillonite PILCS did demonstrate some pH dependence, the lower the pH then the greater the humic acid uptake. Increasing the pH to above 5 seemed to hinder the humic acid uptake. Schnitzer and Khan (1972), have looked at the effect of *d*-spacing and the adsorption of fulvic acid by Na-montmorillonite. It was demonstrated that the interlayer spacings are pH dependent and decrease with increase in pH. It was also suggested that *d*-spacing is related to degree of

ionisation of the functional groups, especially CO<sub>2</sub>H groups in fulvic acid. At low pH relatively few of these groups are ionised and fulvic acid behaves like an uncharged molecule that can penetrate interlamellar spaces and displace water molecules from between the silicate layers of the montmorillonite. As the pH is increased, more functional groups will ionise and result in an increased negative charge. Thus at pH > 5, the *d*-spacing is reduced indicating repulsion of negatively charged fulvic acid by negatively charged montmorillonite.

#### *Ion chromatography*

Ion chromatography was used to see if any leaching of anions occurred from the clays. The results in Tables 3–4 clearly show that for the hydrotalcite samples, a high concentration of nitrate ions were present in the filtrate. This was due to nitrate ions being washed off the hydrotalcite surface, indicating that the samples were coated in a nitrate salt precipitate formed during synthesis and the samples were not sufficiently washed after synthesis. The occurrence of this salt deposit seems to be determined by the method of hydrotalcite synthesis. The presence of sodium carbonate during synthesis helps control the pH and reduce the degree of formation of the sodium nitrate salt deposit. The degree of leaching of chloride ion from the PILCS was expected and appears to be related to the degree of pillaring in the clays.

#### CONCLUSION

The u.v.-absorption results clearly demonstrate the ability of the various clay samples to remove humic substances from upland surface water, either by adsorption or ion-exchange or a combination of these processes. Hydrotalcites proved extremely effective, making use of their anion exchange capacity and interlayer spacings as well as adsorption of humic species onto their surfaces. The PILCS also proved quite effective but to a much lesser extent than the hydrotalcites. This was expected as the PILCS did not possess the ability to undergo anion exchange and also their frameworks were negatively charged and so uptake of humic species was limited to displacement of water in the pillared interlayers and to some degree, surface adsorption. Lower pH values of the exchange slurry tend to improve humic acid uptake, but the PILCS also show a greater time dependence for uptake.

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