



REMOVAL OF TRINITROPHENOL FROM WATER BY A LAYERED DOUBLE HYDROXIDE

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SUMMARY

The aim of this work was to explore the potential use of the hydrotalcite compound $[Mg_3Al(OH)_8]_2CO_3 \cdot xH_2O$, (HT), and its calcined product $Mg_3AlO_4(OH)$, (HT500), as sorbents of 2,4,6-trinitrophenol (TNP). The amounts of TNP removed by HT depends on the pH, whereas those removed by HT500 depends on solid/solution ratio.

Key Words: hydrotalcite, phenols, organic contaminants, sorption, removal, filters.

INTRODUCTION

The increasing level of toxic organic chemicals (TOC) in surface and ground waters coming from diverse human activities is a major concern. Consequently, at present there are many research programs focusing the remediation of pollution from dangerous effluents by degradation or adsorption of TOCs.^{1,2}

The layered double hydroxides (LDH), because they are antitypes of the expandable layer silicates, are potential sorbents for organic chemicals. The LDHs are brucite layers positively charged, $[M^{II}_{1-x}M^{III}(OH)_2]^{x+}$, with interlayer anions $(X^{n-})_{x/n}$, and hydration water molecules, according to the scheme shown in Figure 1. These anions and water molecules can be interchanged by other organic anions and polar molecules. Thus, LDHs, as expandable clay

minerals, have very high internal and reactive surface and are potentially good sorbents for anionic or polar TOCs.^{3,4} On another hand, the hydrotalcite-like compounds have the particularity that its calcined product can rehydrate and reconstruct the original layered structure from water containing anions and thus, can also be potential sorbent for anions from water solutions.

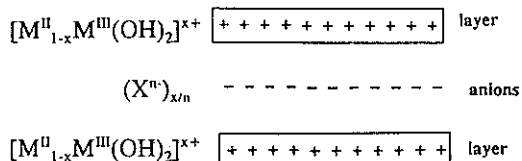


Figure 1. Scheme of the hydrotalcite layered structure.

We recently have reported⁵ a study of the adsorption of trichlorophenol by an LDH and its calcined product that revealed the mechanism of interaction occurring in LDH interlayer surfaces and suggested the possible use of calcined LDH as filters for phenol contaminated waters. In the present work we report the preliminary results of the sorption of trinitrophenol (TNP) on a layered double hydroxide and its calcined product, as looking for the potential use of these compounds as sorbents for phenols from contaminated waters.

MATERIALS AND METHODS

The hydrotalcite compound $[Mg_3Al(OH)_8]_2CO_3 \cdot xH_2O$, (HT), and its calcined product ($500^\circ C$, 24h), $Mg_3AlO_4(OH)$, (HT500), was prepared as described previously⁶.

TNP adsorption on HT and HT500 was measured by batch equilibration technique at diverse solid/solution ratios, pH, and TNP concentrations. The proper amount of solid was weighed in polypropylene centrifuge tubes and the suitable volume of TNP solutions was added. The pH was previously adjusted in the TNP solutions. The suspensions were shaken at $22 \pm 2^\circ C$ and after 24h were centrifuged and the supernatants filtered to determine pH and TNP concentration in the solutions by photometric measurement at 360 nm.

RESULTS

Previous experiments indicate us that HT and HT500 samples removed so quite different amounts of TNP from solution, that the solid/solution ratio used in each case must be different.

The results corresponding to the amounts of TNP removed from solutions by the samples at different solid/solution ratio are summarized on Table 1.

Table 1. Removing percentage of the TNP by the sorbents at different solid/solution ratios

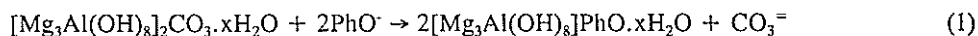
Sample	g/10ml	C _i (μmol/l)	C _e (μmol/l)	% removed
HT	0.02	1000	960	4
	0.05	1000	950	5
	0.10	1000	930	7
Sample	g/30ml	C _i (μmol/l)	C _e (μmol/l)	% removed
HT500	0.02	5000	3875	22.5
	0.05	5000	2062	58.7
	0.10	5000	0	100

The removing power of HT did not change appreciably with the amount of solid in the solution whereas for HT500 it did. From data of Table 1, the 0.05g/10ml ratio for HT and 0.05g/30ml ratio for HT500 were chosen as the best conditions for the present study. These results show much higher removal by HT500 than that by HT. The influence of the pH in the removal of TNP from the aqueous solution is shown in Table 2 for HT and Table 3 for HT500.

Table 2. TNP adsorption on HT at diverse pH (2h, 0.05g/10ml, 1mM)

Sample	pH		TNP concentration, μM		Amount TNP removed %ads
	initial	final	initial(Ci)	final(Ce)	
HT	2.0	6.6	1000	450	55.0
	3.0	7.8	1000	825	17.5
	4.0	8.0	1025	975	4.9
	5.0	8.1	1025	975	4.9
	7.0	8.5	1000	950	5.0
	12.0	11.9	1000	975	2.5

Data in Table 2 indicate that the amount of TNP removed from the solution decreased drastically with the pH. The higher amount of TNP removed by HT at lower pH could be due to the easy displacement of $\text{CO}_3^{=}$ from the interlayer space at this pH, according to the following reaction:

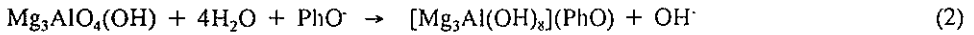


The increase in the pH of the solution observed at lower initial pH should be due to some dissolution of the HT sample.

Table 3. TNP adsorption on HT500 at diverse pH (24h; 0.05g/30ml; 5mM)

Sample	pH		TNP concentration, μM		Amount TNP removed %ads
	initial	final	initial(Ci)	final(Ce)	
HT500	2.0	8.5	4875	1125	76.9
	7.0	11.7	5000	1875	62.5
	12.0	12.0	4750	2500	60.5

Table 3 shows that pH did not greatly influence the amount of TNP removed from the solution by HT500. This removing should occur through reconstruction of the layered structure according to the reaction:



The lower removal found at high pH for HT500 (Table 3) could be explained by the competition between TNP⁻ and OH⁻ species in reaction (2), which also accounts for the increase of the pH observed.

To compare removing power of both sorbents for TNP from aqueous solutions, distribution coefficients (Kd) were determined at two TNP concentrations (5 and 20 mM) according to the expression:

$$Kd = \frac{Cs (\mu\text{mol}/\text{gr})}{Ce (\mu\text{mol}/\text{ml})}$$

where Cs is the amount of TNP adsorbed by unit weight of sorbent and Ce is the TNP concentration in the final solution. Table 4 shows the results corresponding to these values beside the adsorption percentage in each case.

Table 4. Distribution coefficients of TNP in the sorbents studied

Sample	Ci=5μmol/ml			Ci=20μmol/ml		
	Ce	%ads	Kd	Ce	%ads	Kd
HT	2.6	42	135	15.1	20	50
HT500	21	77	2045	162	19	139

Distribution coefficients shown in Table 4 suggest a high adsorbent power for HT and HT500, being the sorbent efficiency higher at low concentration for both sorbents. The higher adsorption capacity was found for HT500 which, at low concentration, was able to remove almost 80% of the TNP in solution. These results suggest that HT and HT500 could be used to eliminate TNP from waters. Taking into account that HT500-TNP

complex can be heated and its calcined product regenerated³, this material could be recycled as filters for TNP contaminated waters. Works on this subject are in progress.

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REFERENCES

1. Zielke, R.C. and Pinnavaia, T.J. 1988. *Clays & Clay Minerals* 36: 403-408.
2. Boyd, S.A.; Shaobai, S.; Lee, J.I. and Mortland, M.M. 1988. *Clays & Clay Minerals* 36:125-130.
3. Sato, T and Okuwaki, A. 1991. *Solid State Ionics* 45:43-48.
4. Hermosin, M.C.; Ulibarri M.A.; Mansour, M. and Cornejo, J. 1992. *Fresenius Environ. Bull.* 1:472-481.
5. Hermosin, M.C.; Pavlovic, I.; Ulibarri, M.A. and Cornejo, J.1993. *J. Environ. Sci. Health A* (In press).
6. Reichle, W.T. 1986. *Solid State Ionics* 22, 135-141.

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