

## Ion exchange properties of sewage treatment plant sludges

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**Digested sludges from sewage treatment plants behave as ion exchangers of the weak acid type. The apparent pK values of the carboxylic and phenol functions, determined by titration, were respectively  $6.03 \pm 0.12$  and  $8.76 \pm 0.25$ . These sludges also fixed metal cations and in particular calcium and barium ions. The phenol functions gave the most stable complexes.**

### Introduction

The sludges, activated and then digested anaerobically, are essentially composed of insoluble humic acids. These acids contain phenol and benzenecarboxylic acid functions [1,2]. It is generally considered that the aromatic rings are polymerized and linked, either directly, or via intermediate aliphatic chains [3]. The average molecular weight varies from 10 000 to 300 000 daltons [4]. In general, the carboxylic and phenol functions are able to exchange ions with the surrounding solution. It is thus interesting to study the ion exchange properties of these sludges from sewage treatment plants, after decantation and filtration [5].

### Experimental techniques

The study was carried out on sludges from the outlet of the belt filter of the sewage treatment plant of Montpellier at la

Céreirède. These activated sludges, from the outlet of the decanter, are treated in an anaerobic digester. They are thus sludges which have been activated, digested and filtered. The exchange kinetics were first studied in order to determine the time necessary to reach equilibrium under the experimental conditions, and the exchange capacities and constants were then determined.

The digested sludges, from the outlet of the belt filter, were homogenized and ground in a mixer, washed in deionized water, then filtered through paper. To determine the exchange capacities, the sludges were titrated with sodium hydroxide, after addition of an excess of strong acid so that all the exchange functions were in acid form. The automatic titrations lasted several hours, to ensure that the equilibria were reached.

For each operation, two identical samples of sludge were taken; one was used for the determination, the other was dried in an oven at 105 °C for 24 hours, then weighed to determine the quantity of dry matter. The constants were then evaluated with reference to the quantity of dry matter of the sludge. The complexation constants with calcium and barium ions were determined by acid-base titration in the presence of an excess of  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  ions respectively. The titration curves were obtained with a "TitraLab" Tacussel. TIM 800 apparatus. The products used were Prolabo RP reagents.

### Results

The times necessary to reach equilibrium were determined by following the changes in a solution containing metal ions

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in the presence of a quantity of sludge in  $H^+$  form. Depending on the samples and the experimental conditions used, the concentrations reached a stable level after about 8 hours for alkali metal ions, 15 hours for alkaline earth ions and several tens of hours for transition metals. These results were taken into consideration for the experimental conditions for studying the ion exchange capacities and constants.

The exchange capacities were determined by slow automatic titration: to a known quantity of washed sludge was added an excess of strong acid and the mixture was titrated with sodium hydroxide. The curves obtained showed three points of inflexion: the first corresponded to the excess of strong acid, the second to the carboxylic function and the third to the phenol function. To be reproducible and reliable, this titration had to be performed over a sufficiently long time (8 to 12 hours). Several curves were obtained to ensure the reproducibility of the results. An example is given in figure 1.

The advantage of determining the capacities by direct titration was to differentiate the carboxylic and phenol functions and to determine their pK. These operations however had the disadvantage of being long, for kinetic reasons. Titration curves were also obtained of the humic acids in the presence of an excess of calcium or barium ions. These showed only a single inflexion corresponding to the carboxylic and phenol functions.

It should be noted that the exchange reactions with alkali metal and alkaline earth ions were much more rapid than with transition metals. In this respect, the curves performed over 24 hours did not show significant differences from those performed over 8 or 10 hours, but the curves obtained in less than one hour were significantly different.

### Discussion

The exchange kinetics of alkali metal ions were relatively rapid (1–3 h) but alkaline earth ions required about 10 hours. The kinetics were even slower for transition metal ions. By operating slowly, it was possible to obtain titration curves for the humic acids contained in the sludges. The interpretation of these curves led to a determination of their ion exchange capacities, distinguishing the contributions of the carboxylic acid and phenol functions. In addition, we were able to determine the pK of each of these functions.

The results obtained show that the exchange capacities are very high, of the same order of magnitude as those observed for ion exchange resins. They are approximately the same for the carboxylic and phenol functions. For the Montpellier sewage treatment sludge, the figures are 1.95 eq/Kg dry matter for the carboxylic function and 1.55 eq/Kg for the phenol function, giving a total capacity of 3.5 equivalents per Kg dry matter.

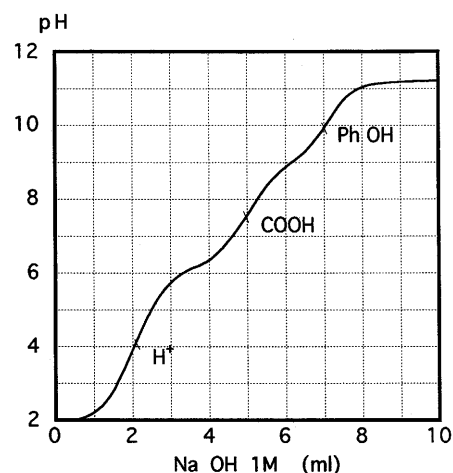


Figure 1. Titration of 5.75 g of raw sludge (25.1% of dry matter) in 120 mL of a  $7 \cdot 10^{-2}$  M solution of nitric acid, by 1 M NaOH. (length of titration ~ 20 hours).

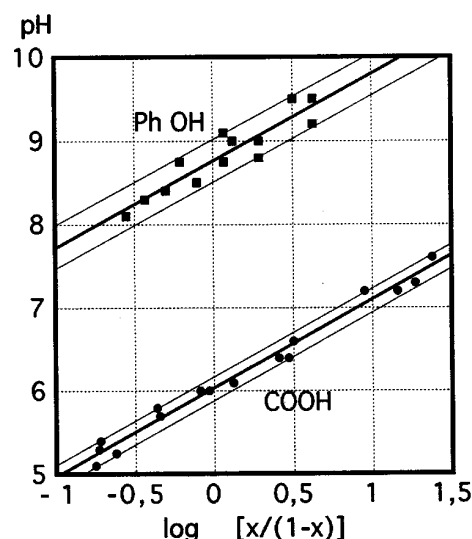
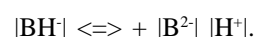
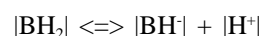


Figure 2. Determination of the acidity pK values of the sludge by titration 1 M sodium hydroxide. (cumulative results over 6 titrations).

It was also possible to determine the pK of each of these functions from the curves. If for each acidity function, we consider the acid-base reaction:



For each acid function, we can write:

$$pH = pK + \log (\text{base} / \text{acid})$$

$$pH = pK + \{ \log x / (1-x) \}.$$

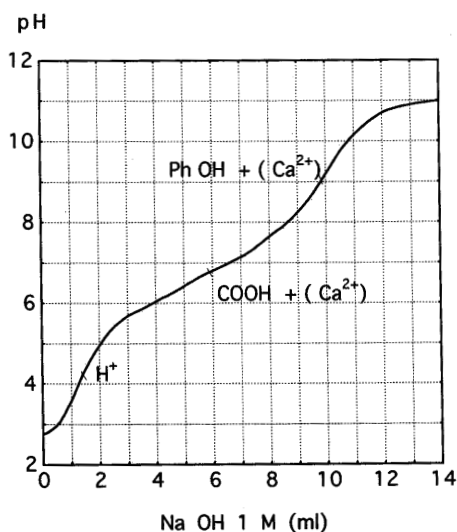


Figure 3. Titration of the sludge in the presence of 2.5 M calcium.

We verified experimentally that the slopes obtained were close to 1. By plotting the curves  $pH = f \{ \log x / (1-x) \}$ , for  $x = 0.5$  we obtained an ordinate at the origin equal to the pK. We found the values of  $6.03 \pm 0.12$  and  $8.76 \pm 0.25$ , for the carboxylic and phenol functions respectively. It is interesting that if we established the number of functions per unit mass, we observed only a single function per ring, and not several as is often indicated for the structure of humic acids.

The presence of ions forming complexes with the sludges at high concentration changes the pK significantly; there is in fact a permutation between these cations and the protons fixed in the sludge, which liberates the latter and increases the acidity of the surrounding solution.

In the presence of an excess of alkaline earth ions, we observed only a single inflexion, for the two acidity functions. This could be due to the formation of mixed complexes between the carboxylic and phenol functions, or, more probably, to a higher stability of the metal complexes with the phenol function. Given that, as for ion exchange with weak acid resins, the stoichiometries observed remain at 1:1, whatever the ion complexed [6], one might think that the phenol function gives more stable complexes than the carboxylic function. The bonds observed are of covalent type and not electrostatic as with the ion exchange resins of strong acid type. The bond lengths are well defined and a polyvalent cation form several bonds at the same time.

The first part of the titration curve, which corresponds to carboxylic function, is little altered. It is thus possible to evaluate the stability of the complex between the alkaline earth ions and each of the functions by studying the two parts of the curve separately.

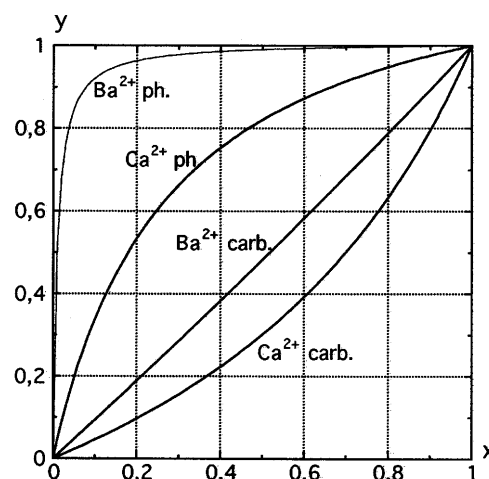
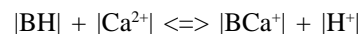
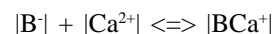
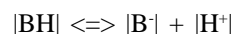


Figure 4. Partition diagram of the  $Ca^{2+}$  and  $Ba^{2+}$  ions between the carboxylic and phenol functions.

Given a 1:1 stoichiometry, we have the equilibria



Which gives the overall constant:

$$K_a / K_c = |BCa^+| \cdot |H^+| / |BH| \cdot |Ca^{2+}|$$

From this we deduce:

$$|H^+| = K \cdot |BH| \cdot |Ca^{2+}| / |BCa^+| = K \cdot |Ca^{2+}| \cdot (1-x) / x$$

$$pH = pK - \log |Ca^{2+}| + \log (1-x) / x$$

with  $pK = pK_a - pK_c$ .

The results, with the slopes of the lines  $pH = f \{ \log (x / (1-x)) \}$ , the pK value found and the corresponding value of K, are given in table I.

Given the approximations and hypotheses made, we can only claim an evaluation of the stability of these complexes and not a true determination. Many other natural phenomena could affect these values; in particular, given the observed stoichiometry, the pK will depend on the anion associated with the metal ion in the resin. However, these values, even though approximate, are sufficient to calculate the variation of the partition coefficients as a function of pH.

A sufficiently soundly based theoretical treatment nevertheless remains possible, and would suffice for prediction of reactions and possible applications.

From the pK values found, it is possible to construct a partition diagram of the calcium and the barium between the solution and the carboxylic and phenol functions in the

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Table I. Stability constants of the complexes with the sludges.

ion	carboxylic function			phenolic function		
	slope	pK	K	slope	pK	K
Ca <sup>2+</sup>	0.948	-0.37	0.43	0.831	0.66	4.57
Ba <sup>2+</sup>	0.986	-0.03	0.93	0.915	2.02	105

sludge. If  $y$  is the ionic fraction of alkaline earth ion in the sludge and  $x$  the ionic fraction in the solution, we have:

$$K = y.(1-x) / x.(1-y)$$

from which  $y = K.x / 1 + x.(K-1)$ .

We observed that these cations essentially fix to the phenol functions and that barium fixes better than calcium. In addition, since the stoichiometry is 1:1, an anion is always associated with the calcium. The fixation of bicarbonate ions seems particularly likely, giving the humic acids an essential role in the calco-carbonic equilibria.

It was not possible to determine the pK for the transition metal cations by this method, since there was interference by precipitation of hydroxides at relatively low pH values. The slowness of the reactions also required very long contact times. Another technique, closer to that for ion exchangers, must therefore be used and performed in batch [7].

### Conclusion

Given these results, we may consider that the fixation of the metal ions on the sewage treatment sludges can be interpreted by the theory of ion exchangers. Other mechanisms of cation adsorption are negligible compared to the strong ion exchange capacities. The exchange parameters are comparable to those for classical ion exchangers, with in particular the exchange constants for the carboxylic functions being of the same order of magnitude as for resins of the same type. On the other hand the exchange kinetics are slower, these depending markedly on the medium conditions: particle size, agitation etc.

It is possible to predict the variation of the partition coefficients from the exchange constants; they vary by a factor of 10 per unit of pH. This is very important, on the one hand for the quality of the discharge water and on the other for the use of the sludges for agricultural spreading. It is also possible to predict that not all soils will have the same sensitivity to heavy metals; in particular these are much more easily assimilated by plants in acid soil than in basic soil [8,9].

The sludges are thus potentially usable for treating solutions containing metal ions, but the maceration time must be sufficiently long.

Water-sediment equilibria and their variation with pH can also be predicted for treatment plants using settling ponds. Daily variations in pH of 1.5 units, currently observed in a settling pond, would correspond to a factor of 30 in the concentration of the metal ions in solution [10]. In fact, for kinetic reasons, the observed day/night variations rarely exceed a factor of 10, which is nevertheless significant. The fact that the concentration of metal ions in solution is higher at the end of the night than at the end of the day is thus a function of exposure to sun, the production of carbon dioxide and the acidity of the medium [11]. In addition, the metal ions can be easily eliminated from the sludges in acid medium (strong acid > 1 molar).

A good knowledge of the equilibria of the metal ions between the water and the sludges would enable the determination of the conditions of retention or release into the environment [12,13].

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