

# PREFORMED FERRIC HYDROXIDE FLOCS AS ADSORBENTS OF HUMIC SUBSTANCES

G. Cathalifaud, M. T. Wais Mossa and M. Mazet

*Laboratoire de Génie Chimique Traitement des Eaux Université de Limoges, Faculté  
des Sciences, 123 Avenue Albert Thomas, 87060 Limoges Cedex, France*

## ABSTRACT

The purpose of this study is to show that previously built floccs obtained by the coagulation-flocculation of kaolinite suspension with ferric chloride are a potential adsorbent of humic substances.

Floccs are prepared from kaolinite ( $< 50 \mu\text{m}$ ) and  $\text{FeCl}_3$  according to the jar-test technique: after 3 minutes of rapid mixing at  $\text{pH} = 5.4 \pm 0.1$ , 30 minutes of slow mixing, humic acids are added for a contact time of 6 hours; the effects of calcium, sodium salts (chloride, sulphate) on the adsorptive capacity of preformed floccs are also studied. The results indicate that the preformed floccs are good adsorbent materials. Langmuir equation is used to determine adsorption capacities.

## KEYWORDS

Water, adsorption, ferric hydroxide floccs, humic substances.

## INTRODUCTION

Humic substances are naturally occurring constituents of sediments, soil and raw water. Much of the reactivity of this organic matter in aqueous solution is attributed to functional groups such as carboxyl, carbonyl, phenolic, methoxyl carboxyl groups which provide most of the negative charge that adds to the mobility of humic substances in the environment; Edwards and Amirtharajah (1985); Mantoura *et al.*, (1978); Vik *et al.*, (1985); Chadik and Amy (1987).

For water treatment, aluminium and iron salts are the most widely used as coagulants and because of the complicated aqueous chemistry of these trivalent metals many researchers disagree about the exact nature of the hydrolysed species and about the mechanism of coagulation-flocculation process. Specific conditions and aluminium and iron species that exist during the charge-neutralization-precipitation-adsorption-ion exchange are often discussed; Dempsey *et al.*, (1985); Randke (1988); Dentel and Gossett (1988); Jekel (1988); Tipping *et al.*, (1988); Hundt and O'Melia (1988); Lefebvre and Legube (1990); Mazet *et al.*, (1990).

The work which is presented hereafter is to study-i) the removal of humic substances by adsorption-precipitation onto previously formed floccs and-ii) the influence of salts on the adsorption capacity and-iii) to discuss the experimental conditions and results.

## MATERIALS AND METHODS

Humic acids (HAc) were prepared from commercial sodium humate (HSc) (Aldrich Chemical Company) according to procedures outlined by Schnitzer and Khan, (1972). (HAc : C % =

51.37 ; H % = 4.19 ; N % = 0.75).  $\text{CaCl}_2$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$  and ferric chloride were of analytical grade as commercialized by Prolabo-France. Kaolinite was provided by KPCL Society (Limoges-France).

Ultraviolet absorption was used to quantify the adsorption of humic materials. Absorbance was measured at  $\lambda = 254$  nm for humic acids with a spectrophotometer (Shimadzu, UV 160) and turbidity by Hach turbidimeter (model Ratio). Before absorbance measurements, the sample was filtered on a  $0.3 \mu\text{m}$  pore diameter filter (Sartorius cellulose nitrate).

The adsorption studies included two parts .

- First of all, coagulation of kaolinite suspension was done with ferric chloride by the jar-test techniques in tap-water ( $\text{pH} = 5.4 \pm 0.1$  ;  $t^\circ\text{C} = 22 \pm 2$  ; ferric chloride =  $25 \text{ mg.L}^{-1}$  ; kaolinite =  $100 \text{ mg.L}^{-1}$  ; rapid mix : 3 min. at 150 RPM ; slow mix : 30 min. at 50 RPM). The flocs are used as adsorbents for the adsorption studies.

- Secondly, the adsorption tests proper, which consist of adding known concentrations of HAC to the prebuilt flocs suspension still under slow mixing in the jar-test conditions. After equilibrium time (6 hours) the suspension is filtered and analysed. Measured absorbances are then converted to residual concentrations according to standard curves.

Salts are added to prebuilt flocs suspension still under slow mixing, then after 30 minutes the HAC are added for the adsorption test.

\* The pH is adjusted with dilute base (NaOH 0.2 N) or dilute acid (HCl 0.1 N).

\* The  $\text{Fe}^{3+}$  residual concentration is determined by the AFNOR NFT 90-017-juin 1982 method (limit  $50 \mu\text{g.L}^{-1}$ ) and by atomic absorption.

\* Zeta potential is measured by using Pen-Kem Laser Zee Meter, model 500 L.

The Langmuir equation best describes the experimental results obtained in this study despite the heterogeneous surface of preformed flocs. We have used the linearized form :

$$(\Gamma)^{-1} = (\Gamma^\infty)^{-1} + (\text{Cr.K}.\Gamma^\infty)^{-1}$$

$\Gamma$  : adsorption capacity for a given adsorbate ( $\text{mg.g}^{-1}$ )

$\Gamma^\infty$  : maximal adsorption capacity ( $\text{mg.g}^{-1}$ )

Cr : residual adsorbate concentration at equilibrium ( $\text{mg.L}^{-1}$ )

K : thermodynamic constant of adsorption ( $\text{L.mg}^{-1}$ ).

## RESULTS AND DISCUSSION

Figure 1 indicates both the variation of adsorption capacity as a function of pH and the variation of residual  $\text{Fe}^{3+}$  concentration. These results show that the flocs preparation and the Cad/m values are maximum at  $\text{pH} = 5.4 \pm 0.1$  ( $\text{HAc} = 10 \text{ mg.L}^{-1}$ ).

The quantity of residual ferric ion as a function of slow mixing time lies between  $< 0.050$  and  $0.120 \text{ mg.L}^{-1}$ , pH variations are 5.4 and 6.10 for flocs only case; pH non variation is obtained when the experiment is controlled by nitrogen gas.

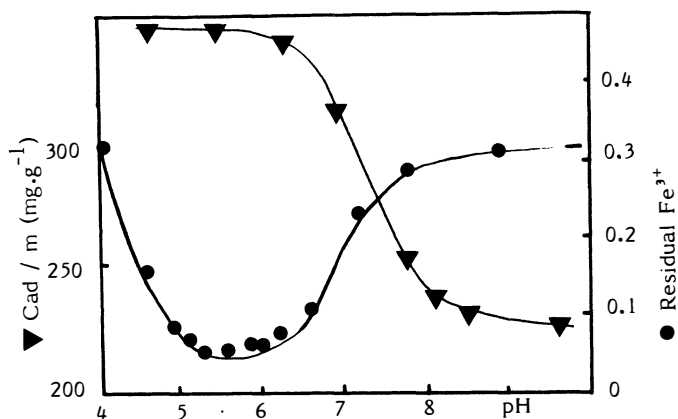


Fig. 1 : Variation of adsorption capacity of HAC ( $10 \text{ mg.L}^{-1}$ ) onto prebuilt flocs and residual ferric ion versus pH (contact time 6h)

Figure (2) indicates the adsorption capacity of **HAc** onto prebuilt ferric hydroxide flocs without or with presence of different salts (saturation curve).

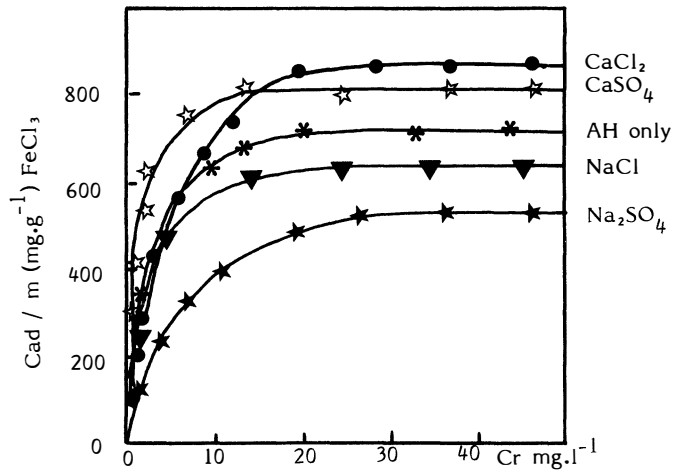


Fig. 2 : Adsorption isotherms of humic acids onto prebuilt flocs only and with different salts (saturation curve)

After linearization of the Langmuir equation, the maximal capacity of adsorption ( $\Gamma^\infty$ ) for **HAc** onto prebuilt flocs and the constant  $K$  in presence of salts are given in table (I).

Table I Adsorption capacity of **HAc** onto preformed ferric hydroxide flocs only and also in presence of different salts.

Nature of salts added	concentration <sub>1</sub> mmol.L <sup>1</sup>	$\Gamma^\infty + 30$ (mg.g <sup>-1</sup> )	$K(Lmg^{-1})$
<b>HAc</b> only	-	710	0.517
CaCl <sub>2</sub> , 2H <sub>2</sub> O	0.5	860	0.446
	1.5	1000	0.401
	2.5	1200	0.487
CaSO <sub>4</sub>	0.5	800	1.038
	0.75	990	0.938
	1.25	1050	1.005
NaCl	0.44	660	1.355
	1.21	625	0.934
Na <sub>2</sub> SO <sub>4</sub>	0.22	550	1.183
	0.66	500	1.593

If the influence of sodium ions is negligible, the results indicate that when calcium ion concentration **increases the adsorption capacity increases**. The influence of sulphate ions is to decrease the adsorption capacity.

Figure 3 indicates the evolution of zeta potential for preformed flocs **as a function of contact time** after adding the humic acids(10 mg.L<sup>-1</sup>).

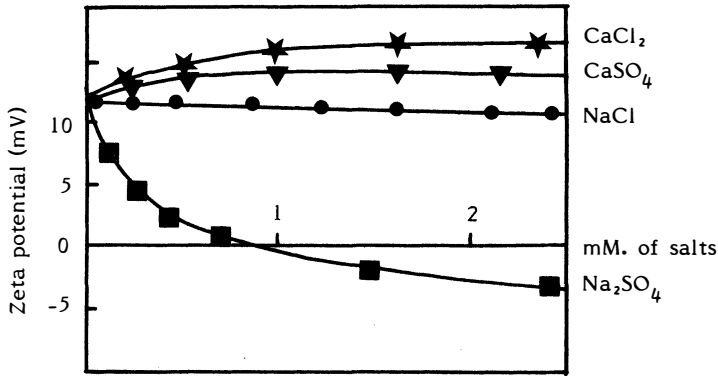


Fig. 3 : Variation of zeta potential of floc particles versus contact time

The zeta potential measurements show that probably at least two mechanisms take place in the adsorption phenomenon which is possible only at the surface of the flocs (Wais Mossa and Mazet, 1990). One mechanism is rapid (4-5 min) and involves an attraction between the positive charges of the flocs and the negative charges of the humic acids (precipitation) corresponding approximately to the half of the initial concentration of HAc (figure 3) : the mechanism can be schematized by the relation (1).

The second mechanism will be slower and may involve an exchange reaction consisting of the flocs giving up hydroxide ion for anionic sites of the organic substances (humic acids). The mechanism may be schematized by the relation (2) and accounts approximately for the other half of the initial concentration (HAc).

This work's results indicate-i) that humic and fulvic acids are able to adsorb onto metallic hydroxide flocs principally during coagulation-flocculation process and-ii) that in the classical coagulation stage, the neutralization and reversal of colloid charge may be caused partially by precipitation of colloids onto the surface of microscopic positively charged metal hydroxide.

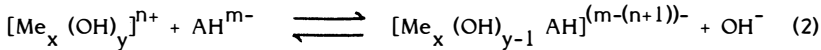
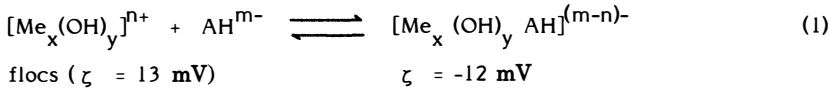


Figure 4 shows that the variation of zeta potential is a function of quantity of salts added to the preformed flocs suspension.

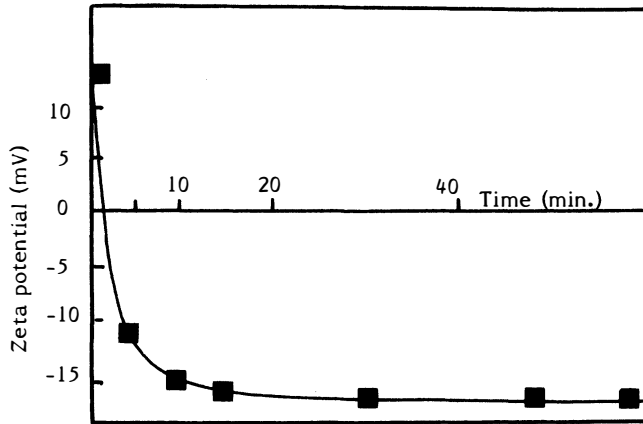
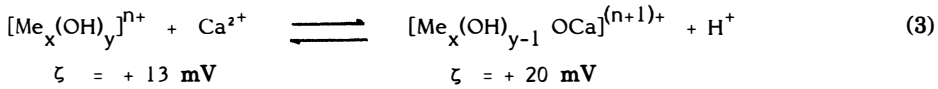


Fig. 4 : Variation of zeta potential of prebuilt flocs with salts quantity added

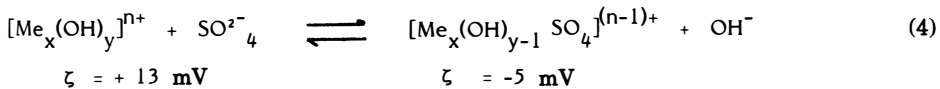
The results indicate that calcium ions have a more important effect on the zeta potential of preformed iron hydroxide floc particles and so on the adsorption capacity of flocs for humic acids. This result is in good accordance with the Mustafa and Ikramul Hag (1988) results for adsorption of  $Ca^{2+}$  on amorphous iron hydroxide. The addition of sodium ions has no effect, but the sulphate ions decrease both the value of zeta potential ( $\zeta = -5$  mV) and the adsorption capacity of flocs; the same results are obtained by Sigg and Stumm (1981) for adsorption of sulphate onto goethite.

The mechanisms which are proposed for calcium and sulphate ion additions can be written as the following relation.

\* Adsorption of calcium ions onto preformed flocs :



\* Adsorption of sulphate ions :



The mechanism proposed for calcium ion interactions on the surface of metallic hydroxide flocs is illustrated by figure 5. The shift of the isoelectric point for flocs from pH = 7.3 to pH = 8.7 shows that calcium ions are chemically adsorbed at the surface of the flocs.

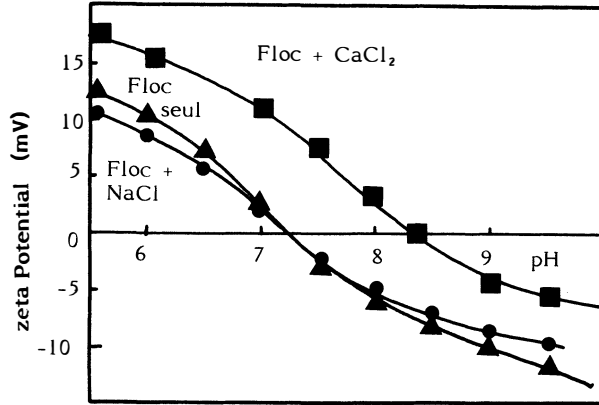


Fig. 5 : Zeta potential variation of preformed hydroxide flocs as a function of pH (after 30 min. of slow mixing)

## CONCLUSION

Prebuilt ferric hydroxide flocs obtained by coagulation of kaolinite with ferric chloride have very good adsorption characteristics for humic acids.

If sodium ions have no effect, calcium ions increase the adsorption capacity of flocs. Sulphate ions decrease the adsorption capacity by a **competitive adsorption** mechanism with humic acids. The possible mechanisms of adsorption are first : an interaction between the flocs (positive charges) and humic acids (negative charges) giving an adsorption-precipitation of **HAc** onto flocs and second : **an exchange of ions** between hydroxide ions of hydroxide flocs and anionic humic acids.

This work's results indicate-i) that natural polymeric compounds in water are able to adsorb onto metallic hydroxide flocs **principally during coagulation-flocculation** process and-ii) that in the classical coagulation stage, the **neutralization** and reversal of colloid charge may be caused partially by interactions with microscopic positively charged non-soluble metal hydroxide.

## REFERENCES

- Angbo L., Mazet M., Wais Mossa M.T. (1990). Jönköping, Sweden, 23-26 April and Water Supply, **8**, 87-91.
- Chadik P.A., Amy G.L. (1987). Environ. Technol. Letters, **8**, 261-268.
- Dempsey B.A., Sheu H., Tanzeer T.M., Mentink J. (1985). J. Am. Water Works Assoc., **77**, 3, 74-80.
- Dentel S.K., Gossett J.M. (1988). J. Am. Water Works Assoc., **80**, 4, 187-198.
- Edwards G.A., Amirtharajah A. (1985). J. Am. Water Works Assoc., **77**, 50-57.
- Hundt T.R., O'Melia C.R. (1988). J. Am. Water Works Assoc., **80**, 176-186.
- Jekel M.R. (1986). Water Res., **20**, 1535-1542.
- Lefebvre E., Legube B. (1990). Water Res., **24**, 591-606.
- Mantoura R.F.C., Dickson A., Riley J.P. (1978). Estuarine and Coastal Marine Science, **6**, 387-408.
- Mazet M., Angbo L., Serpaud B. (1990). Water Res., **24**, 12, 1509-1518.
- Mustapha S., Kramul Hag (1981). Environ. Technol., **2**, 311-316.
- Randtke S.J. (1988). J. Am. Water Works Assoc., **80**, 40-56.
- Schnitzer M., Khan S.V. (1972). Marcel Dekker inc., New York.
- Sigg L., Stumm W. (1981). Colloids and Surface, **2**, 101-117.
- Tipping E., Woof C., Backes C.A., Ohnstad M. (1988). Water Res., **22**, 5, 321-326.
- Vik E., Carlson D., Eikum A., Gjessing E. (1985). J. Am. Water Works Assoc., **77**, 58-66.
- Wais Mossa M.T., Mazet M. (1990). Environ. Technol., **12**, 51-58.