INHIBITION OF COAGULATION PROCESS BY FORMATION OF COMPLEXES BETWEEN CYANOBACTERIAL PEPTIDES/PROTEINS AND COAGULANT

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INTRODUCTION

The efficient removal of AOM (Algal Organic Matter) by coagulation requires sufficient particle destabilization at a pH value at which coagulants (Al/Fe hydrolysing salts) bear the highest charge and the organic macromolecules provide the most active centres (Duan and Gregory, 2003). It was ascertained that due to their high affinity with metal ions, several AOM peptides/proteins inhibit coagulation by the formation of highly soluble metal-peptide/protein complexes (Bernhardt et al., 1985; Takaara et al., 2005). This leads to an increase in dissolved/colloidal Al or Fe that cannot be effective in the coagulation process (Ma et al., 2012). This study is aimed at the description of inhibition effect of peptides/proteins isolated from cyanobacterium *Microcystis aeruginosa* on coagulation by formation of complexes with Fe.

METHODOLOGY

Peptides/proteins were characterized by DOC, molecular weights and isoelectric points (p*I*). Complex forming peptides/proteins were detected using affinity chromatography. Fe-peptide/protein binding capacity was evaluated by standard jar tests performed under different pH conditions and initial DOC concentrations. Ferric sulfate was used as coagulant. The amount of Fe bound in peptide/protein dissolved complexes was determined as a difference in Fe concentration after filtration through a 0.22 μm membrane filter and through an ultrafiltration membrane of 1000 Da.

RESULTS

The results of jar tests (Fig. 1) demonstrated that the lowest residual protein/peptide (DOC) concentrations were achieved at pH 4-6 for all initial DOC concentrations. At pH 6-7, a noticeable increase in residual DOC and iron concentrations was observed. It was ascertained that this increase is caused by formation of surface complexes between dissolved or microcolloidal Fe and peptide/protein deprotonated carboxyl groups ($-COO^-$) by means of a coordinate electrostatic interaction.

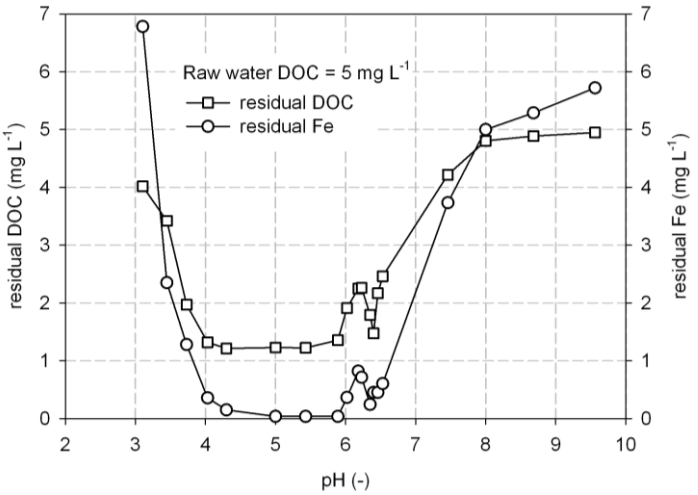

Fig. 1. Dependence of residual DOC and residual Fe on pH value for initial DOC concentrations of 5 mg L^{-1}.

Fe-peptide/protein complexes can be formed only when sufficient amount of carboxyl groups (-COOH) present in peptide/protein side chains is deprotonated and Fe is positively charged. The connection between complex formation and charges of Fe-hydroxopolymers and peptide/protein functional groups implies that

the peptide/protein binding capacity (BC) for Fe depends on pH value. The highest BC (1.38 mmol of Fe per 1 g of DOC) was found at around pH 6.2. The influence of pH on the amount of iron incorporated in organic matter and conditions of Fe-peptide/protein surface complex formation are shown in Fig. 2. The ascertained values of peptide/protein p*I* indicate that at pH < 5.5 (average p*I*) the positive charge of complex forming peptides/proteins predominates. Positively charged peptides/proteins and Fe-hydroxopolymers repel each another and the formation of Fe-peptide/protein complexes is insignificant. At pH 5.5-7.5, the complex formation considerably increases due to the attractive electrostatic interaction between peptide/protein deprotonated carboxyl groups (-COO^-) and positively charged Fe-hydroxopolymers. At pH > 7.5, iron occurs as anionic hydroxocomplexes, e.g. $[Fe(OH)_4]^-$, and peptides/proteins are negatively charged. Thus, the formation of Fe-peptide/protein complexes is reduced owing to the electrostatic repulsion between iron compounds and peptides/proteins.

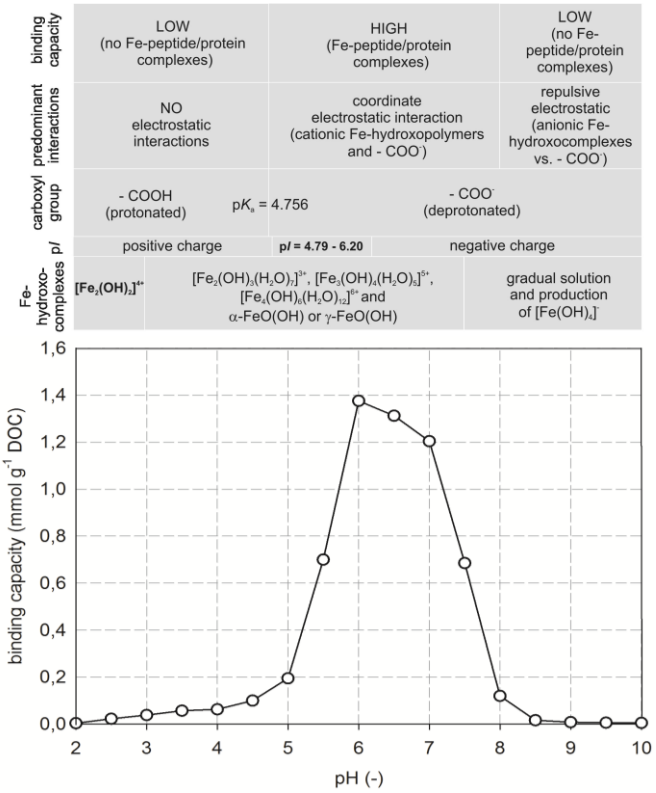

Fig. 2. Description of Fe binding capacity as a function of pH and charge characteristics.

CONCLUSION

It was found that the coagulation inhibition caused by formation of coagulant-peptide/protein complexes is dependent on pH. The maximum amount of Fe incorporated in complexes with cyanobacterial peptides/proteins was found at pH about 6. Therefore, to reach the maximum removal of cyanobacterial peptides/proteins by ferric coagulants, it is necessary to lower the coagulation pH below 6.

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