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# The influence of additives ($Ca^{2+}$, $Al^{3+}$, and $Fe^{3+}$) on the interaction energy and loosely bound extracellular polymeric substances (EPS) of activated sludge and their flocculation mechanisms

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ABSTRACT

The activated sludge (AS) flocculability markedly improved after the addition of $Al^{3+}$ and $Fe^{3+}$ compared to $Ca^{2+}$ at a concentration of 2 mEq/L. Though the energy barrier decreased about 30% when $Ca^{2+}$ was added, the AS flocculability did not improve substantially. This indicates that extended DLVO theory can explain AS flocculation with $Al^{3+}$ and $Fe^{3+}$ as additives but is not appropriate for $Ca^{2+}$. In addition, no matter which cation was added, the AS flocculability was highly correlated to the loosely bound extracellular polymeric substances (LB-EPS) content. The majority of added $Ca^{2+}$ remained in the bulk solution (about 92%), whereas almost all of the $Al^{3+}$ and $Fe^{3+}$ added was found in the pellet (about 98%). The cation' ability to bind to the AS is closely related to the energy barrier and LB-EPS contents, therefore it is the core reason behind the AS flocculation changes observed upon the addition of multivalent cations.


## 1. Introduction

The activated sludge (AS) process is commonly adopted in most wastewater treatment plants (WWTPs), and the effluent suspended solids (ESS) are strongly affected by the performance of AS flocculation and settling (Schmid et al., 2003). Increases in the quantity of ESS not only lead to increases in pollutants like chemical oxygen demand (COD), total nitrogen (TN), and total phosphate (TP), but also to heavy metals and potential pathogens (Chang et al., 2006). Thus, improvements in AS flocculability and settleability will have a major impact on the effluent quality.

AS is composed of various microorganisms that are sensitive to environmental conditions; thus, almost any fluctuation (such as temperature and organic load) in the surrounding system can cause changes in the physical, chemical, and biological properties of AS. Therefore, the flocculation mechanisms of AS are much more complex than those of typical colloidal particles. All commonly recognized intermolecular interaction theories have been used to explain the binding of AS entities (Wilen et al., 2000), such as polymer bridging, Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, hydrophobic interactions, multivalent bridging theory, and steric interactions (Wilen et al., 2000; Sobeck and Higgins, 2002; Sheng et al., 2010).

Classical DLVO theory is often used to interpret colloid stability and to describe the microorganisms and AS flocculation. It is also thought that the interaction energy calculated according to this theory has a considerable effect on AS flocculation (Sobeck and Higgins, 2002; Liu et al., 2007). The total interaction energy ($W_{tot}$) in classical DLVO theory involves energy contributions from the Van der Waals force ($W_A$) and electric double layer ($W_R$). Later, contributions from Lewis acid–base interactions ($W_{AB}$) were added to extended DLVO theory (Wu et al., 1999). Thus $W_{tot}$ in extended DLVO theory can be expressed as: $W_{tot} = W_R + W_A + W_{AB}$. The microbial flocculability and the contributions of extracellular polymeric substances (EPS) to AS aggregation were also recently explained by extended DLVO theory (Liu et al., 2008, 2010).

Furthermore, each of the aforementioned flocculation theories emphasizes the importance of EPS because, firstly, they mainly accumulate on the cell surface (Yuan et al., 2011) and hence will always be involved in interactions between flocs and, secondly, EPS are the critical organic part of AS (Park and Novak, 2007) and as such determine the physical and chemical characteristics of AS (Morgan et al., 1990). Because of the vital importance of EPS, many studies have focused on EPS in order to understand the mechanisms underlying AS flocculation and dewaterability. Most investigators believe that surface properties, surface charge, EPS composition, and the hydrophobicity of AS, rather than the quantities of EPS, govern its flocculability and settleability (Liao et al., 2001; Ni

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