



## Review

# Influence of polyelectrolytes and other polymer complexes on the flocculation and rheological behaviors of clay minerals: A comprehensive review



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## ABSTRACT

Separation of clay minerals from industrial wastewaters is of great academic and practical importance. Current treatment techniques are either not economically viable, not environmentally friendly, or both. Thus, researchers are actively trying to develop optimal and more environmentally friendly wastewater treatment processes. Clay minerals like montmorillonite, bentonite, kaolinite and illite have numerous applications in various industries including, mineral processing, cosmetics, pharmaceuticals, paint, dyes, cement, concrete, functional fillers, paper making, clarification of wines and oils, water treatment and improving drilling mud properties. Their wide applications increased the volume and treatment complexity of water contaminated with them since they form highly stable suspensions in water. Flocculating agents such as polyelectrolytes have the potential to separate the above-mentioned minerals from industrial wastewater effluents. Polyelectrolytes are more effective and environment-friendly flocculants, in contrast to inorganic metal salts and some non-biodegradable synthetic polymers that pose serious hazards to human health and the environment. The development of polyelectrolytes is considered to be among the most important breakthroughs in solid–liquid separation processes, which have resulted in an improved treatment of water polluted with minerals. In the characterization of clay mineral separation using polyelectrolytes, it has been common practice in the past to either emphasize on the flocculation behavior of colloidal clay–polyelectrolyte suspensions (i.e., settling behavior or floc sizes) or on the behavior of networked clay–polyelectrolyte suspensions (i.e., filterability or dewaterability of sediment). However, flocculation and rheological parameters, which are very important factors in optimizing the wastewater treatment process, have rarely been reported in the literature. The aim of this paper, therefore, is to offer a comprehensive review of the state-of-the-art contributions for polyelectrolyte systems, focusing on the development of different types of polyelectrolytes and their applications in flocculating and dewatering clay minerals. Electrokinetics and rheological behavior of different clay minerals using different polyelectrolytes are critically evaluated. The effect of several parameters related to the clay mineral (type, composition), the polyelectrolyte (e.g., synthetic/natural, molecular weight, charge type, charge density, linear vs branched) and the flocculation medium properties (e.g., pH, ionic strength, clay mineral and polyelectrolyte concentration and type) are reviewed. This paper provides up-to-date progress in the treatment of water contaminated with clay minerals using various polyelectrolytes. The gaps and potential parameters of investigation in flocculation optimization studies are identified and more economical and environmentally friendly reagents in wastewater treatment are highlighted.

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## 1. Introduction

Clay minerals are primarily phyllosilicate minerals characterized by their layered structures of tetrahedral silica sheets associated with aluminium based octahedral sheets, exhibiting a plate-like morphology. These minerals occur in nature as a result of weathering of silicate minerals [1]. Application of clay minerals has been immensely significant and widespread in various industries for many decades due to their abundance and inexpensiveness. Kaolinite, illite, montmorillonite and bentonite are the most common clay minerals of commercial significance. Their applications are primarily determined by the physical characteristics, mineral composition and cation exchange properties. These minerals are utilized in agricultural applications [1], pharmaceuticals [2,3], food industry, construction, cosmetics [1,4–6], oil and gas drilling fluids [6–9] paints and dyes [4–6,10], papermaking industry [11], environmental remediation [1] and water treatment [4–6].

Large amounts of clay minerals present in wastewater discharged from industrial activities such as mineral processing, papermaking and sludge dewatering. The presence of clay minerals in wastewater leads to the formation of highly stable clay-water dispersions. In mineral processing industries, high content of clay minerals in ores generate several impediments in leaching and milling techniques. Clay minerals are often washed off from mineral ores using copious amounts of water, producing huge quantities of highly stable clay-water suspension [12]. Clay minerals like bentonite also adversely affect coal floatation processes by decreasing froth stability. Furthermore, paper and pulp industries heavily contribute to the production of colloidal suspensions of kaolinite utilized as fillers to enhance paper quality. The fine

kaolinite particles are insoluble, form persistent suspensions in water and require aggregation to remove them from water by implementing solid–liquid separation techniques [13]. Additionally, the treatment of clay suspensions produces large amounts of sludge comprising up to 97% water content apart from the settled fine clay mineral particles. Sludge handling and dewatering is one of the foremost concerns in wastewater treatment processes and, thus, intensive research has been dedicated to optimize the dewatering processes of sludge while reducing ecological footprint and the costs involved. Discarding such highly stable and concentrated clay dispersions into water bodies without proper treatment causes severe ecological problems. For example, high water turbidity and high colloidal particle concentrations have been reported to adversely affect feeding habits of numerous aquatic species. This was accompanied by a sizeable reduction in the types and numbers of fish species [13,14].

Clay particles are very fine and possess a net surface charge that induces electrostatic repulsions between the particles enhancing their stability in dispersions. Treatment of wastewater contaminated with clay minerals primarily targets the separation of these minerals, which form persistent suspensions, making wastewater treatment a major challenge for many industries. Several techniques have been employed to treat colloidal wastewaters based on different principles. These methods include solvent extraction, precipitation, flotation, coagulation, flocculation, ion exchange, membrane filtration, adsorption and electrolysis. However, coagulation–flocculation remains the most commonly utilized technique for colloidal wastewaters in industries due to its simplicity, effectiveness and versatility. Coagulation–flocculation techniques primarily deal with destabilizing the suspensions by introducing chemical agents that induce a solid–liquid separation

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