

EROSION OF COLLOIDS COATED WITH HUMIC SUBSTANCES IN FIXED AND FLUIDIZED BEDS

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Abstract. Migration of various pollutants associated with colloidal particles has been reported by several researchers. Detachment of colloids and their associated pollutants could be controlled by hydrodynamic as well as chemical conditions of the eroding water. The objective of this study is to understand the mechanisms of detachment of uncoated colloids and colloids coated with humic substances from relatively coarse media grains. Under fixed-bed conditions, the percent detachment was found to increase with an increase in pore velocity. Increased organic coatings caused percent detachment to decrease under fluidized bed conditions. The results of this study will be useful for modifications to soil erosion models for cohesive sediments and estimation of transport of contaminants carried by colloids during dredging operations.

INTRODUCTION

Humic substances which are present in almost all natural waters can alter the fate and transport of numerous contaminants and colloidal matter. When humics coat particles, they not only stabilize the particles but enhance the diversity of binding sites for pollutants and alter particle-particle and particle-surface interactions as well. A few studies have been completed recently on the detachment of "clean" colloids from "clean" surfaces (Amirtharajah and Raveendran, 1993; Sharma et al, 1992; and Khilar and Fogler, 1984). Colloidal surfaces in nature are seldom "clean", and coatings of humic substances are almost always present on these particles. The objective of this research is to study the detachment of colloids coated with humics from coarse media grains with changes in water chemistry.

Applications of Research. This research will help explain the phenomenon of detachment and migration of colloids coated with humics and their associated

pollutants from coarse bed sediments found in natural water bodies and aquifers. The results of this study will also extend to modifications of soil erosion models for cohesive sediments and estimation of transport of contaminants carried by colloids during dredging operations.

BACKGROUND

Natural organic matter is a mixture of many organic solutes and macromolecules. Different compounds of such a complex mixture display different behavior in binding with contaminants, colloids and surfaces. The possible binding mechanisms with the surfaces and colloids include cation exchange, protonation, anion exchange, water bridging, cation bridging, ligand exchange, hydrogen bonding and Van der Waals forces. Some of these mechanisms are more prevalent and some create stronger bonds, depending upon specific conditions. The main polyvalent cations responsible for the binding of humic and fulvic acids to soil clays are Ca^{2+} , Fe^{3+} , and Al^{3+} . Cation bridging through Ca^{2+} has been reported as an important bridging mechanism by various researchers (Amirtharajah and O'Melia, 1990; Schnitzer and Khan, 1972; Stumm and Morgan, 1981).

Different humic materials can show different degrees of adsorption, which can be explained by their difference in composition and polarity. Various researchers have reported preferential adsorption of large humic molecules (Davis and Gloor, 1981; Jekel, 1986; Jardine et al, 1989). The adsorption of humics decreases with decreasing aromatic carbon content and increasing oxygen to carbon ratio (Zhou et al, 1994). Low desorption rates have consistently been found for high molecular weight fractions, and hence the chemical nature of adsorption could be expected for such adhesion (Zhou et al, 1994). There are obviously much less negative charges in the larger molecules, which should favor adsorption (Jekel, 1986). The effective

stabilizing (adsorbed) fraction is predominantly uncharged, forming a layer similar to the nonionic polymeric stabilizers used widely in dispersion technology. Experiments show that a poly(vinylalcohol)-(vinylacetate)-copolymer, behaves like fulvic acid (Jekel, 1986). Humics are able to adsorb on mineral surfaces like kaolinite, even though they bear the same electrical charge (Wershaw, 1991; Zhou et al, 1994).

Experiments on detachment of polystyrene particles coated with cationic polyelectrolytes from both uncoated and coated glass surfaces with the same polymer showed higher forces were necessary for the release of the particles when compared with uncoated polystyrene particles (Varenes and Van De Ven, 1988). If excess polymer is present, it can form additional bonds between the coated particles and the glass surface, or prevent escape by enlargement of polymer segments connecting the particles and the surface. By coating the glass surface or coating both the particles and the glass surface with cationic polyelectrolytes, the shear rate required to detach polystyrene particles from the glass surface was found to be greatly increased (Varenes and Ven de Ven, 1988). In another study, pretreatment of cellulose and glass surfaces with cationic polyelectrolytes greatly increased the forces needed to detach titanium hydrous oxide spheres (Hubbe, 1987).

MATERIALS AND METHODS

Standard particles. In order to simulate natural conditions, Suwannee River humics were used to coat kaolinite particles used in this study. These "standard" coated particles were prepared by equilibrating kaolinite clay with a pre-determined dosage of humic substances under controlled conditions of ionic strength, pH, temperature and time. In order to study the adsorption of humics, an electrolyte of ionic strength 0.01M was prepared using calcium nitrate, and 300 ml equal portions were decanted into teflon-capped glass bottles. Different amounts of humics were added to these portions, and the pH was adjusted slightly above neutral. Equal amounts of kaolinite clay were then added, and the suspension was shaken for 24 hours. Finally, the total organic carbon was determined using a "Dohrmann 180" carbon analyzer.

Detachment experiments. Standard coated particles were filtered through a packed bed of soda-lime glass spheres manufactured by the Potter Industries, Parasipany, NJ. The glass beads were equilibrated as

described by Rajagopalan and Chu (1982) in order to keep the surface chemistry the same during each experiment. This was accomplished by immersing glass beads in 4 liters of electrolyte solution having the same pH and ionic strength as that of the suspension influent, but without addition of humics.

A glass column of 27 mm i/d was packed with 175 g of equilibrated glass beads and tapped thoroughly until no further settlement was observed. The influent was filtered for 4 hours followed by a backwash. The chemistry of the backwash water was adjusted in individual experiments. The percent detachment (as mass) was determined by mass balance.

RESULTS AND DISCUSSION

Figure 1 shows the adsorption of humic substances on kaolinite particles. The amount of organic carbon adsorbed on the surface of kaolinite particles was found to increase with an increase in solution phase concentration until a saturation value of around 1% by weight of kaolinite was reached. High molecular weight fractions of the humic substances adsorb preferentially as reported by several researchers (Davis and Gloor, 1981; Zhou et al, 1994; Jekel, 1986; Jardine, 1989).

The detachment experiments done under fluidization conditions with 20% bed expansion showed a decrease in percent mass detached with an increase in organic coatings on particles. The results from two different series are shown in Figure 2. The detachment of

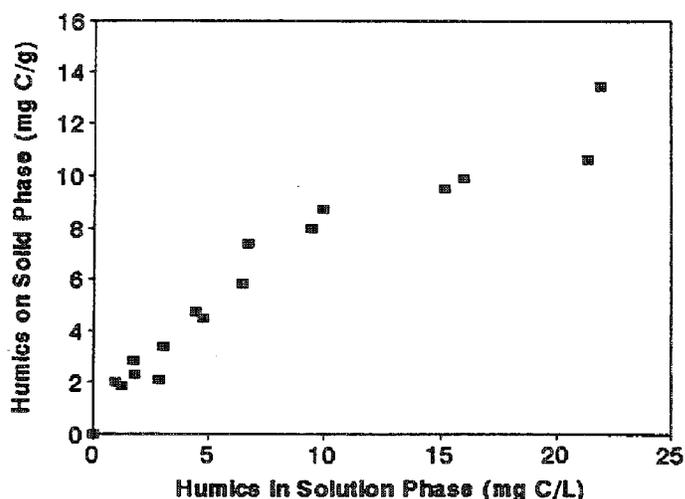


Figure 1. Humic substances coating on kaolinite.

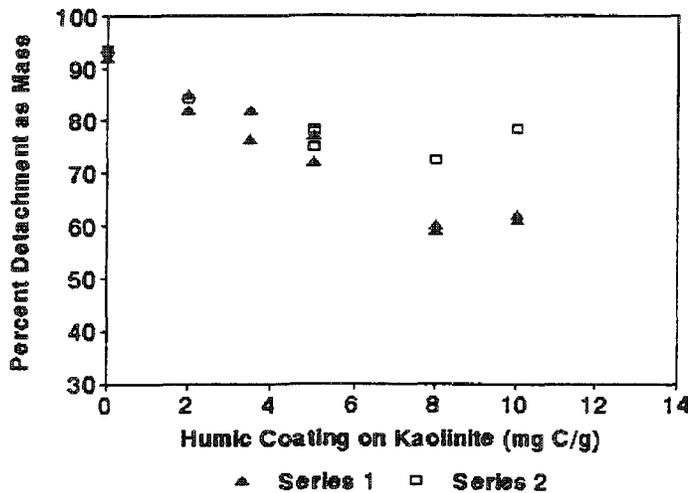


Figure 2. Effect of organic coatings on detachment.

uncoated kaolinite particles was found to be 90-95%, which decreased as the organic coatings were increased. Varennes and Van de Ven (1988) in stagnation point experiments on detachment of latex particles from a glass surface showed that by coating glass surfaces (or both the particles and the glass surface) with cationic polyelectrolyte, the shear rate required to detach polystyrene particles from the glass surface was greatly increased. In another study, pretreatment of cellulose and glass surfaces with cationic polyelectrolytes greatly increased the forces needed to detach titanium hydrous oxide spheres. The force of adhesion for coated particles was as much as 30 times greater than the highest value obtained in the absence of polymers. The hydrodynamic shear stress required for detachment was found to increase with treatment level, molecular mass, and decreasing cationic charge of the polymer (Hubbe, 1987).

Stabilization of particles (or coatings) is caused primarily by the favorable uptake of high molecular weight neutral components of the humic substances, forming a layer similar to the non-ionic polymeric stabilizers used widely in dispersion technology (Jekel, 1986). Observations made in this study are consistent with those in the literature on polymer bridging.

The release of uncoated kaolinite particles under fluidization conditions with 20% bed expansion was found to be insensitive to ionic strength variations (using CaCl₂) over three orders of magnitude as shown in Figure 3. The detachment of natural sediments collected from the Calcasieu River bed near Lake Charles, LA, was also found to be insensitive to similar

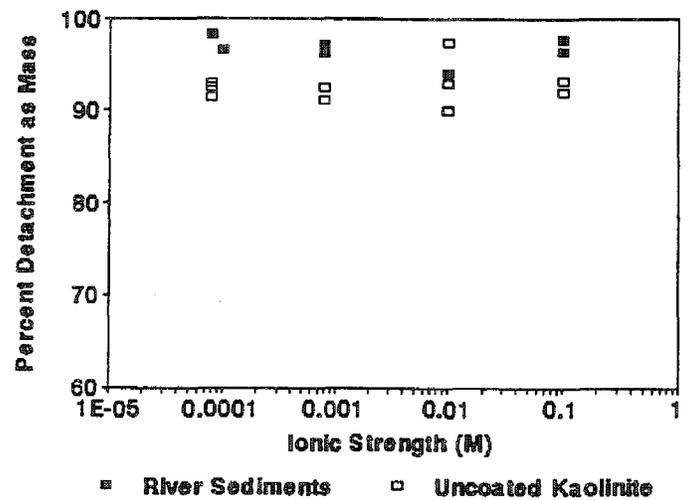


Figure 3. Particle release under 20% fluidization.

variations in backwash water ionic strength. The percent detachment of Calcasieu River sediments was found to be higher than the kaolinite particles. The Calcasieu River sediments and kaolinite detachment experiments were both done at pH 7.2. At this pH the edge charge on kaolinite is zero (Kia et al, 1987) and only the face charge is present. If the charge on a particle is low then the effect of ionic strength could be insignificant because of weak electrostatic interactions. Ryan and Gschwend (1994) showed that a decrease in ionic strength in the presence of colloids with opposite charge

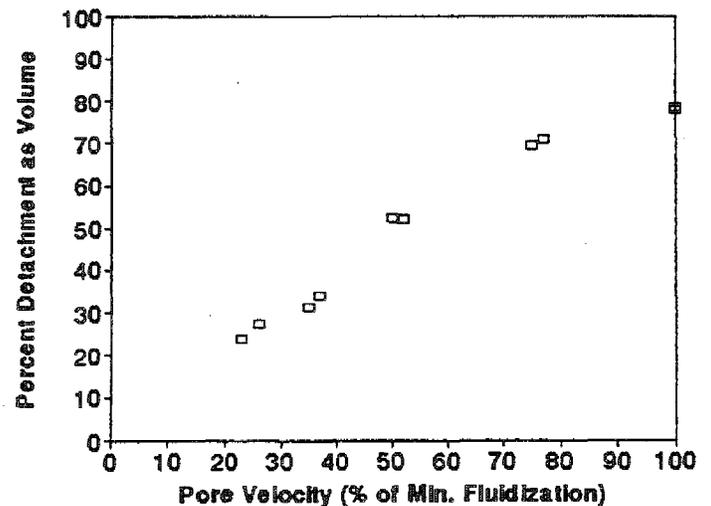


Figure 4. Kaolinite detachment as a function of pore velocity.

(kaolinite and Goethite at pH 4.8) did not cause a significant increase in the clay release rate. This was attributed to the strong interactions between oppositely charged kaolinite and Goethite, mitigating the effect of ionic strength on the double layer forces between the colloids (Ryan and Gschwend, 1994).

The effect of pore velocity on particle detachment under fixed-bed conditions is shown in Figure 4. These experiments show percent detachment as volume. Particle size analysis was performed using a Brinkmann Particle Size Analyzer model 2010. Solids volume (as cc/ml) was determined in the influent, effluent and backwash streams rather than mass measurements, and the ratio of volume of particles detached to the volume of particles attached was then calculated. Figure 4 shows that an increase in pore velocity causes detachment to increase. It is surmised that an increase in pore velocity causes shear stress to increase and hence causes a higher percent detachment.

CONCLUSIONS

The following conclusions are drawn from this research.

1. The amount of organic carbon adsorbed on the surface of kaolinite particles was found to increase with an increase in solution phase concentration until a saturation value of around 1% by weight of kaolinite was reached.
2. The percent mass detached decreased with an increase in organic coatings on the particles.
3. The release of uncoated kaolinite and Calcasieu River sediments was found to be insensitive over three orders of magnitude variation in backwash water ionic strength.
4. Under fixed-bed conditions, the percent detachment increased with an increase in the pore velocity.

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