Effect of cations traces on the flocculation process of low clay concentrations using nonionic polyacrylamide flocculants

M. Abd El Latif
Fabrication Technology Dept., Institute of Advanced Technology and New Materials, Mubarak City for Scientific Research and Applied Technology, Alexandria, Egypt
Email: amona1911@yahoo.com

The effect of cations traces presence on the flocculation process of clay from industrial wastewater using both prepared and commercial nonionic polyacrylamide flocculants have been studied. Different factors affecting the flocculation process including flocculant dose, agitation time and pH of the medium in the presence of Na^{+} ions have been investigated in details. Finally, the efficiency of the prepared flocculant has been compared with one of the commercial flocculant.

تم دراسة تأثير وجود الكميات الضئيله من الايونات الموجبةالمختلفه على عملية تجميع الطفلـه العالقـة فـى ميـاه الـصرف الصناعى. كما تم دراسة تاثير بعض العوامل على عملية التجميع مثل تركيز ايون الصوديوم , كمية المادة المجمعـه و زمـن التقليب و حموضة الوسط فى وجود ايون الصوديوم باستخدام كلا من المادة المجمعة المحضرة و التجاريـة و مقارنـة نتـائج تجميع كلا منهم.

Keywords: Polyacrylamide, Flocculation , Traces cations, Clay suspension, Nonionic flocculant

1. Introduction

The purpose of water clarification is to remove the suspended particles and colloidal materials from wastewater. Dense suspended solids such as sand can be easily removed by sedimentation. Problems in clarification begin with less dense suspended particulate matter and the colloidal materials. Small, less dense particulate matter may be removed by sedimentation only with extended detention times not available in many situations. Colloidal materials form very stable water suspensions [1]. Colloidal particles may consist of clay, silica, iron and other heavy metals, color and organic solids. Colloidal particles have large surface area in relation to their mass. This makes them very reactive; in clays, this reactivity is shown as an electrostatic attraction of cations. Colloids can exist in water as either suspensions (dispersed) or as gels (flocculated). The nature of the colloidal clay particle (hydrophobic) means that clay will flocculate if allowed to [2].

The efficient solid-liquid separation of clay suspensions is of critical importance to porcelain, white ware, and refractories industries. A variety of reagents may be added to slurries to enhance sedimentation by inducing aggregation. Salts of multivalent cations that effectively reduce the surface charge of the solids are termed coagulant while high molecular weight water-soluble polymers that are sufficiently large to bridge between particles are termed flocculants [3]. The more concentrated the salts (electrolytes) present with clay suspension the more likely it is that clay will flocculate. All soluble salts have this affect, like (sodium chloride). Cations adsorbed onto the clay surface allow the clay to flocculate even when the total salt concentration is low. The cations adsorbed onto the surface of the clay particle can greatly affect how the clay behaves. The cations act as a link between the clay particles. The binding force onto and between the clay plates is dependent on a number of factors including:

- The charge of the cations;
- The size of the cations including their hydration shell; and
- The thickness of the double layer outside the surface of the clay particles [2].

The strength of the bond depends on the cations present. Sodium ions have a single positive charge; their clay-binding ability is poor. Calcium ions have a double positive charge; their clay-binding ability is good. Magnesium is intermediate because, although it has a double positive charge like calcium, when hydrated it is larger than a hydrated calcium ion.

The performance of a flocculant in any application (measured in term of supernatant clarity) is decided by the complex interplay between a numbers of factors, many of which have been reviewed include:

• Slurry properties such as clay particles size, presence of traces ions of salts, and pH.
• Physical properties of the flocculant, such as molecular weight.
• Dynamic aspects of aggregate rupture and formation under applied agitation speed.

2. Materials and experiments

2.1. Materials

1. Acrylamide was supplied by Fluka chemicals Co. Ltd. (Switzerland), assay ≥ 99%. Potassium persulphate [$K_2S_2O_4$] supplied by S.D.S. FINE-CHEM Ltd. (England), min assay 98%, chloride not more than 0.04%.
2. Sodium chloride was supplied by BDH laboratory, England & Calcium chloride was supplied by AVONDALE laboratories, England & Copper sulphate was supplied by ADWIC company & Lead nitrate was supplied by BDH laboratory, England & Ferric chloride was supplied by Fluka chemicals Co. Ltd. (Switzerland).
3. Clay powder, Egyptian highly refined Ball clay (smectite- vermiculite) powder of very fine particle size, used mainly for manufacturing refractory bricks and mortar, was obtained directly from Alexandria for Refractories Company. The physical and chemical characteristics of the material (data provided by the manufacturer) are as shown in table 1.
4. MAGNAFLOC7025, is a high molecular weight nonionic polyacrylamide flocculants (Ciba Specialty Chemicals, U.K) are supplied as a free flowing granular powder, its properties as follow: (physical form: white granular powder, particle size: 98% < 1000μm, bulk density: 0.8g/cm3, pH of 1% solution at 25°C: 5.5, viscosity at 25°C of 0.5% solution at shear rate 5.11: 50 cP, relative viscosity at 25°C: 4.1)

Table 1
Characterization of clay powder

Particles size	- 325 mesh
Moisture	1% maximum
Silica	51.4%
Alumina	32%
Ferric oxide	2.6%
Titania	2%
Calcium oxide	0.3%
Sodium oxide	0.1%
Magnesium oxide	0.12%
Potassium oxide	0.08%
Loss on ignition	11%.

2.2. Preparation of polyacrylamide

The preparation conditions were 6% monomer concentration, 0.001M potassium persulphate, and polymerization time 4hours at 50°C using solution polymerization technique.

The procedure of polymerization is described elsewhere [4]. All of acrylamide monomer converted to polyacrylamide of relative viscosity 8٠.5 at 25°C using 0.5% solution.

2.3. Preparation of clay suspension

Clay suspensions were prepared from clay powder immediately before each set of experiments, through mixing clay powder with 800ml of distilled water.

2.4. Preparation of flocculant solution

A concentrated flocculant solution was prepared by first wetting the surface of the flocculant (0.5g) with 3ml of ethanol, and complete until 100ml with distilled water. The sample then stirring for 2 hours to have a homogeneous 0.5%(w/v) solution that stored as stock solution.

2.5. Jar test

1. The prepared clay suspension was put in each of five 1L beakers and stir for two minutes at 190 rpm using Laboratory Flocculator (Flocumatic 6PLAZAS/samples) model- 3000914 (J.P. Selecta Co.), which consists of six-spindle multiple stirrer units with stainless steel paddles, in order to assure complete dispersion of clay in water. Afterwards, a settling time of 10 min was allowed.

2. At the end of the settling period, the sample for turbidity measurement was withdrawn using automatic pipette from a height of 3 cm below the surface of each beaker. These samples measured using 2100 p Turbidimeter (Hach Co.) calibrated using standard suspensions.
3. Add different concentrations of Na^+ ions (0.072,0.144,0.719,1.438 mg Na^+/liter of clay suspension) followed by the required amount of 0.5% polyacrylamide solution to each test suspension.
4. Immediately after the addition of the salts and flocculants, the suspension was stirred at a uniform speed of 75 rpm for 2 min this was followed by a slow stirring at 25 rpm for 5 min.
5. The stirrer was then switched off and the flocs allowed settling undisturbed for 10 min.
6. The residual turbidity of the supernatant liquid was measured as described previously.
7. For studying the effect of suspension pH in the presence of Na^+, clay suspension was adjusted at the desired initial pH using (0.1M HCL & 0.1M Na_2CO_3). pH variation was 2-10. pH monitored using pH-meter (Denver Instrument Co., U.S.A.).

3. Results and discussion

3.1. Effect of presence of traces salts with clay suspension

Different cations which might possibly present in the water used commercially to prepare the waste suspension were tested for their effect on the flocculation efficiency of clay suspension. Table 2 represents the effect of $5X10^{-3}$gmole cations on the residual turbidity of 0.25% clay suspension flocculated using 10mg/l (mg flocculant/liter clay suspension) of 0.5% polyacrylamide flocculants.

From this table it is noticed that the flocculation behavior of clay suspension slightly affected with the presence of different types of cations. It can be seen that the flocculation efficiency shows a little tangible increase with addition of salts especially using $FeCL_3$. This is due to addition of salts into clay suspension would compress the electronic double layer around the particle and the particles become more adjacent and agglomerated together and settled faster [5]. Also a gradual decrease in residual turbidity is noticed as the valence of cations increase. This is returned to flocculation influences of the type of cations adsorbed onto the negative surface of clay through formation of clustering of clay particles into micro aggregates where the type of cations act as a link between the clay particles. The strength of this link depends on the type of cations present. Sodium ions have a single positive charge; their clay-binding ability is poor. Ferric ions have a triple positive charge; their clay-binding ability is good. Calcium, copper and lead ions are intermediate because they have a double positive charge [6]. It is apparent for the same cation valency that there is a direct relation between the ionic radii (molecular weight) of cation and its agglomeration ability.

3.2. Effect of sodium chloride concentration

The aggregation efficiency of low concentrations of Na^+ was studied both in the presence and absence of flocculant, using different concentrations of clay suspensions. It is clear from fig. 1 that there is a decrease in the residual turbidity as the cation concentration is increased. But the residual supernatant suspension still turbid due to the low concentration of salt studied. This returned to the coagulation of clay suspension using cations take place through double-layer compression. The ions that are opposite in sign to the net charge on the surface of the particles enter the diffuse layer surrounding the particle. If enough of these counter ions are added, the diffuse layer is compressed, reducing the energy required to move two particles of like surface charge into close contact [7]. Destabilization by double-layer compression is not a practical method for water treatment, because the salt concentrations required for destabilization may approach that of seawater and, in any case, the rate of particle aggregation would still be relatively slow in all but the most concentrated suspensions.

So the effect of variation Na^+ concentration on the turbidity removal of different clay concentration solutions was studied using

Table 2
Effect of salts on the flocculation

Salts	Without salts	NaCl	$CaCl_2$	$CuSO_4$	$Pb(NO_3)_2$	$FeCl_3$
	Residual turbidity (NTU)					
Prepared flocculant	131	128	107	105	102	100
Commercial flocculant	33	32	27	25	25	23

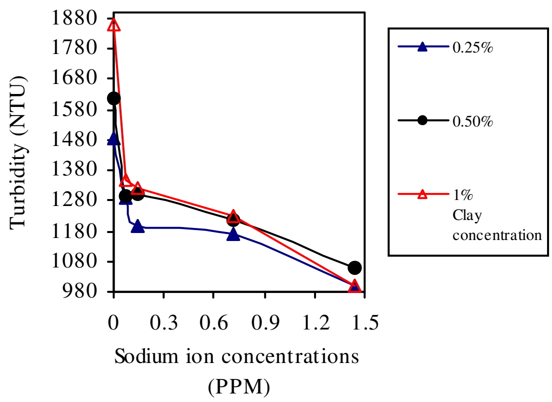

Fig. 1. Effect of sodium chloride concentration on residual turbidity volume of clay suspension=800m1.

10ppm of 0.5% polyacrylamide flocculant. Fig. 2 illustrates the obtained results using prepared and commercial polyacrylamide flocculant consequently. It is interested to notice that the flocculation efficiency of the prepared polyacrylamide flocculant improved with addition of Na^+ up to 0.144ppm for both 0.25% and 0.5% clay concentration and 0.719ppm for 1% clay concentration, beyond these concentrations, no further improvement of the flocculation process has been observed. It is worthy to mention here that with addition of 0.144ppm Na^+, the turbidity has been reduced by 15%, 30% and 20% for clay concentration suspension 0.25%, 0.5% and 1% respectively. This result implies the existence of direct relation between the clay concentration and the cations concentrations using fixed flocculant dose. Optimum Na^+ concentration for each clay suspension concentration should be explored. On the other hand, concerning to the commercial flocculant, no significant effect of Na^+ addition on the efficiency of the flocculation process has been observed. This is may be explained by taking into account the particles size of suspended clay at such range of turbidity which is very small, so the effect of NaCl addition is almost nil. It is interesting to mention here that the residual amounts of suspended clay in the case of using prepared and commercial flocculant, in the absence of NaCl, are 0.57gm and 0.11gm respectively from initial 8 g. this in addition to the fact that the molecular weight of prepared flocculant is double of the commercial one. The combination of these two factors explains the obtained behavior.

3.3. Effect of flocculant dosage

The effect of the floculant dose using Na^+ concentration (0.144 ppm) on the residual turbidity was studied. Fig. 3 ilustrates that the residual turbidity decreases as the flocculant dose is increased. This is due to increasing the flocculant materials adsorbed on different supended clay particles and help particles to aggregate into clusters that is settled rapidly leaving clear supernatant suspension.

Also it can be seen that the addition of flocculant has a little effect on the residual turbidity up to dose in excess of 6.25ppm. It is mean that 6.25ppm of 0.5%flocculant solution is sufficient to flocculate 800ml of clay suspension in the presence of 0.144ppm Na^+.

3.4. Effect of suspension pH

The effect of pH variations was investigated using the previously determined selected flocculation conditions. It is clear from fig. 4 that the residual turbidity increased as the suspension pH is increased from 4 to 10.

This may be due to the fact of the negative natural surface of clay particles. Increasing pH results in increasing the negative charge on the edges of clay layers [2] and when two charged surfaces are brought together their

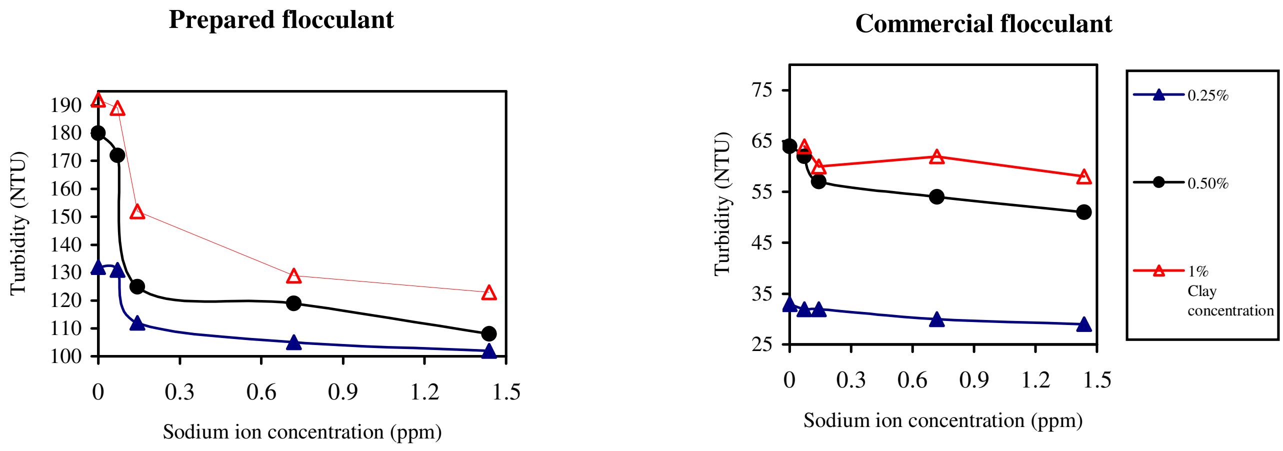

Fig. 2. Effect of sodium chloride concentration and polyacrylamide flocculant on residual turbidity for different clay concentration flocculant dose=10ppm; volume of clay suspension = 800m1.

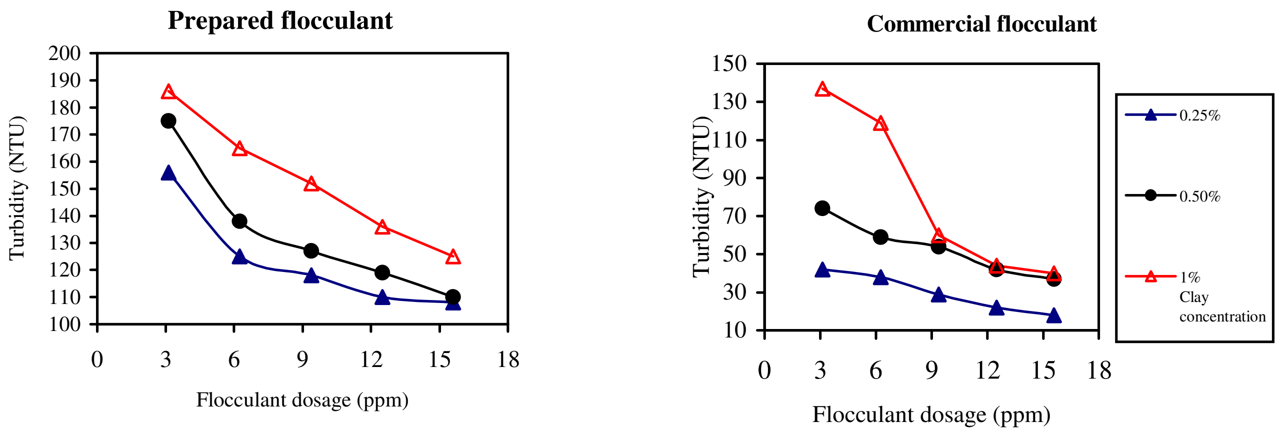

Fig. 3. Effect of flocculant dosage on residual turbidity for different clay concentration Na^+ concentration=0.144ppm, volume of clay suspension = 800m1.

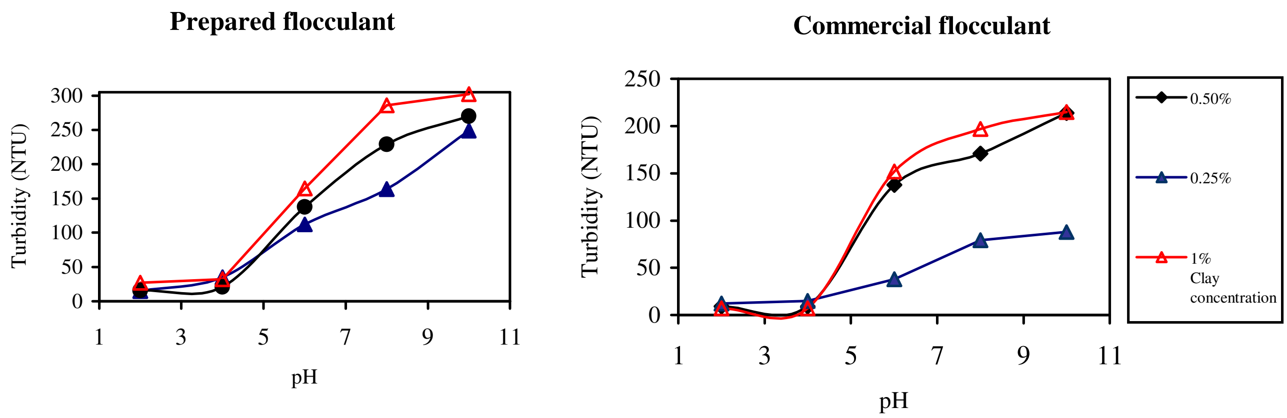

Fig. 4. Effect of suspension pH on residual turbidity Na^+ concentration =1.144ppm, flocculant dose=6.25ppm; volume of clay suspension =800m1.

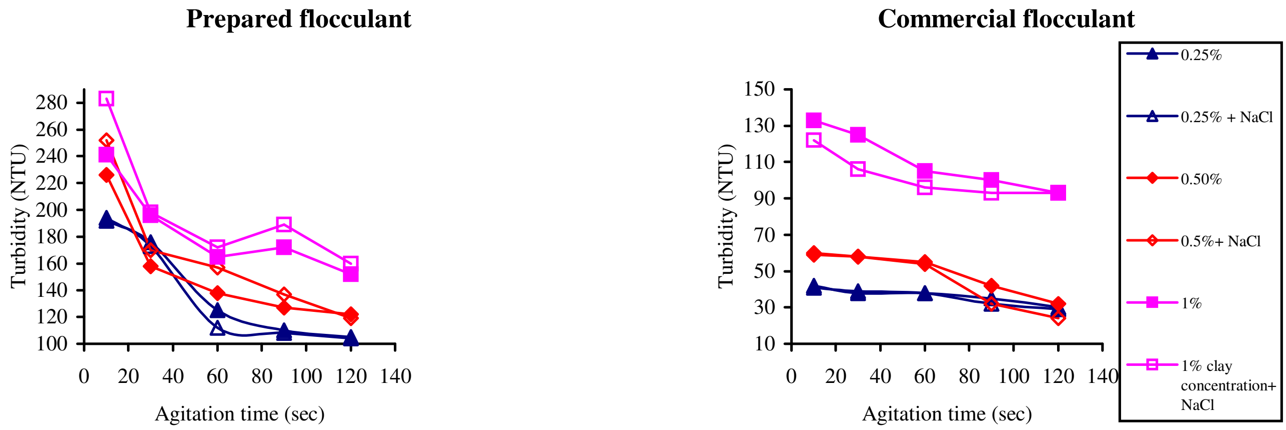

Fig. 5. Effect of agitation time on residual turbidity for different clay concentration Na^+ concentration =0.144ppm, flocculant dose=6.25ppm; volume of clay suspension =800m1.

diffused layers overlap, an electrical force would exist between the two surfaces and for surfaces with similar charges [8] repulsive force exists. The magnitude of this repulsive force is related to the magnitude of charge on the particles, as this charge increased the repulsive force is increased; this is by its role increases the stability of clay suspension, so increase in pH increases the charge density on clay particles and this in turn increases the dispersion of clay particles in suspension and bridging flocculation become more difficult. The previous results reveal that the solution at pH 2 has the highest flocculating compatibility [5]. These results are in agreement with Chandra W.A., et al. [9]; they studied the flocculation of kaolin as a function of pH.

3.5. Effect of agitation time in the presence and absence of NaCl traces

To examine the impact of the agitation time on the flocculation of clay suspensions, the previously determined flocculant dose and Na^+ concentrations were used to determine the optimum time of agitation at 75 rpm for both flocculants of study.

From fig. 5, it can be seen for the two cases that the applied agitation time had a major effect on the extent of aggregation achieved. It is noticed continuous decrease in the supernatant turbidity with increasing the agitation time until 60sec then any further increase in agitation time led to a minor decrease in the turbidity, so the optimum agitation time that is sufficient to brought the solid surface close enough together and London-van der waals forces over-power the repulsion forces is one minute in the two cases studied. Furthermore a little reduction on turbidity obtained in case of using NaCl with the flocculant. Because the presence of traces Na^+ ions will assist the aggregation of clay particles in the suspension by reducing the net surface charge of the particles in the suspension. As the net surface charge is decreased, the thickness of the diffused layer surrounding the particles is reduced and the particles become more adjacent and agglomerated together [7].

4. Conclusion

The presence of cations traces have slight effect on the flocculation process efficiency of clay from industrial wastewater using commercial flocculant. On the other hand, using the prepared flocculant, it was found that the variation of Na^+ concentrations has a positive effect on flocculation process. The turbidity has been reduced by about 20-30%, depending on the clay concentration using the optimum Na^+ concentration. Both of the flocculant dose and the pH was found of pronounced effect which the turbidity affected dramatically. One minute of agitation at 75 rpm were found enough to reduce turbidity in significant way.

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