Preparation of polyaluminum chlorides containing nano-$\text{Al}_{13}$ from Egyptian kaolin and application in water treatment

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ABSTRACT: In this study, a novel approach to metakaolin dealumination to produce aluminum chloride from Egyptian kaolin has been described and the prepared aluminum chloride can be used to produce polyaluminum chlorides (PACs) with various basicities (B = OH/Al values). The prepared PACs which contain $\text{Al}_{13}$ ($\text{[AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$) was investigated using XRD and colorimetric method. In XRD spectra, a strong $\text{Al}_{13}$ signal appeared in the range of 2θ from 5 to 25° (Wang, 1999). Jar test was performed to test the coagulation efficiency and a comparative study was achieved between different coagulants as alum, $\text{AlCl}_3$, PAC and PAC–$\text{Al}_{13}$ with various basicities in treating actual water samples. PAC–$\text{Al}_{13}$ with highest content of $\text{Al}_{13}$ has more turbidity removal, and achieves the highest charge-neutralizing ability than alum, $\text{AlCl}_3$ and PAC under the study conditions. The dosages from 5 to 25 mg/l were used in the comparative studies.

Keywords: polyaluminum

INTRODUCTION

The raw material for the manufacture of aluminum chloride, i.e. ‘bauxite’, has been discovered in Egypt in limited amounts. It is natural to look for the production of this important material through other available resources of raw materials that contain high alumina and low iron oxide contents. One of the numerous aluminous raw materials distributed on a large scale in Egypt is the kaolinitic clays. Several sintering and acid-extraction processes have been investigated for the production of alumina from kaolin and other clays. Bakr and El-Abd described in several papers the extraction of alumina from Egyptian kaolin by hydrochloric acid leaching (Bakr et al., 1969; Ibid, 1967). The effect of acid concentration, reaction temperature, calcination temperature, leaching time and acid/clay molar ratio on the extraction process was investigated.

The calcination temperature was the most important parameter affecting the extraction process followed by reaction temperature. Other literature on the extraction of alumina from clay by hydrochloric acid treatment include the work of Ziegenbalg et al. (1983), Poppleton and Sawyer (1977), Eisele et al. (1980) and Shanks, et al. (1986). The prepared aluminum chloride from the kaolinitic clay may be used as a coagulant to remove the turbidity; however, it has problems due to its high coagrestitivity that may lead to problems in usage and storage. Several research efforts have been devoted to improve the efficiency of coagulation–floculation process; a basic and essential treatment technique in water and wastewater treatment facilities was used.

After studying the chemistry and behavior of simple aluminium salts (i.e. conventional coagulants, such as alum), the way of the improvement seemed to be the partial polymerization of them. The result of these efforts was the production of a range of pre-polymerized aluminum solutions, referred to as polyaluminum chlorides (PACs) with variable degrees of polymerization. These products are used extensively all over the world, especially during the last two decades, with increasing demand. Their properties were intensively examined and have proved to be more efficient in lower dosages and higher pH, temperature and colloids range, than the conventional ones, leading to cost and operative effective treatment (Sinha et al., 2004; Tchobanoglous, 2005). PAC shows excellent properties in the coagulation–floculation processes in the presence of $\text{Al}_{13}$ $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}]^{7+}$, which is also called
Al\textsubscript{b} (Tang and Luan, 1995). Besides, the characteristics of higher positive charge and strong binding ability to aggregates, they are temporary refractory to hydrolysis before adsorbing the particle surfaces. In fact, the pre-produced PAC is an intermediate product in the controlled processes of hydrolysis, polymerization, gelatin and precipitation for aluminum species. Thus, industrial PAC of high Al\textsubscript{13} content has been the main aim of research and production (Pasrthasarathy and Bu, 1985).

Polyaluminum chloride (PAC) may be produced by adding a base to aluminum chloride until an empirical formula of Al(OH)\textsubscript{n} Cl\textsubscript{3-n} (with n from 1 to 2.2) is achieved. A variety of species can be formed when stock solutions of PAC are added to raw water. O’Melia and Dempsey (Melia et al., 1982; Dempsey et al., 1985), in a review of work done using a wide variety of PACs coagulants, proposed that some PACs formulations may contain aluminum precipitates the positively charged precipitates of Al(OH)\textsubscript{3} may improve flocculation kinetics in turbidity removal and adsorb humic substances. Based on the analysis of re-dissolved precipitates, solubility test, turbidity data and electrokinetic measurements, Van Benschoten concluded that alum and PAC precipitate to form different solid phases; the polymeric structure remains intact within the PAC precipitate and particles are more positively charged and produce lower turbidity than for alum floe (Benschoten et al., 1990).

O’Melia et al. concluded that PAC coagulants are effective at lower dosages than other aluminum preparations for the coagulation of high turbidity waters, particularly at low temperature or acidic pH, also that PAC is an effective filter aid for low turbidity waters, providing for destabilization and subsequent filtration of particles at acidic and neutral pHs (O’Melia et al., 1989). The main aim of this work is to produce PACs with various basicities contain Al\textsubscript{13} from Egyptian kaolinitic clay.

**Figure 1. Leaching system**

**MATERIALS AND METHODS**

**Materials**

The clay sample selected for investigation was kaolinitic clay obtained from Sinai at El–Tih. Stock hydrochloric acid from Merck Company (37%) was used. Stock solutions containing 1.0 and 0.1 mol l\textsuperscript{-1} Al were prepared with a reagent-grade AlCl\textsubscript{3}.6H\textsubscript{2}O in CO\textsubscript{2}-free distilled and demineralized water. Sodium hydroxide
solutions were freshly prepared by dissolving reagent grade NaOH pellets in distilled and demineralized water and were standardized against standard HCl solutions.

**METHODS**

**Grinding**

The average size of the raw local clay sample was about 2 to 3 inches in diameter. The clay sample was ground using a ball mill to -200 meshes.

**Calcinations experiments**

Ground clay sample with particle size-200 mesh was subjected to calcination. A muffle furnace (Thermolyne) with a maximum temperature of 1500 °C was used. The calcination temperature was performed from 500 °C to 700 °C.

**Acid leaching experiments**

10 grams of the clay samples with particle size -200 mesh were leached using different acid concentration (2N to 8N) for different periods of time (2 to 12 hours), at different leaching temperatures (50 °C to 90 °C) and acid/clay ratio (6:1 to 14:1) w/w using a constant temperature shaking water bath at a fixed shaking rate of 160 cycles/min and using boiling under reflux; Fig.1 shows leaching apparatus. By the end of leaching process, the resulting slurry was filtered to separate the undissolved materials. The produced cake was washed three times with 30 ml portions of distilled water. The filtrate and the washings were collected and separated. The resulting solutions were diluted, analysed for aluminum ion using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer) Model Vista PRO. The effects of leaching period, leaching temperature, acid concentration on the extraction were investigated.

**Preparation of polyaluminum chloride (PACs)**

PAC was synthesized by titrating one liter solution of aluminum chloride 0.1 mol l⁻¹ Al with 5 mol l⁻¹ NaOH in the reactor, to obtain ligand numbers (n) of 1.0, 1.5, 2.0 and 2.2. The rate of base addition in every case was 0.09 ml min⁻¹. All the prepared PACs solutions were clear at the end of the titration. A pH electrode was inserted through one inlet and another one through which high purity N₂ gas was bubbled through the solution. The aperture at the tip of the capillary was less than 0.15 mm in diameter to minimize diffusion of the aluminium solution into the capillary during mixing. A stainless shaft with propeller stirrer was inserted in another port for mixing of solutions (parthasarthy, 1985). The solution temperature in the reactor was maintained at 25 °C by circulating temperature controlled water through the jacket of the reaction vessel. All the PAC samples were characterized using the timed calorimetric method, and XRD (wang, 1999).
Jar test procedures for coagulation test
The jar tests were conducted using a standard procedure involving a rapid mixing at 120 rpm for 1 to 2 min followed by a slow mixing at 20 to 35 rpm for 20 min and 20 min sedimentation. The supernatant solution was withdrawn and used for the measurement of turbidity, Total Organic Carbon (TOC) and pH.

Colorimetric test for characterization PACs
The nature of the monomeric, polymeric, and solid aluminum hydroxide species can be measured using timed colorimetric speciation techniques such as the ferron test. The fraction of Al designated as Alₐ, which reacts with Ferron almost instantaneously (0–1 min), is assumed to include primarily monomeric species. The species that react with Ferron rapidly but slower than Alₐ (1–120 min), Alₐ, are thought to include polynuclear Al species of superior quality and possess structures that are fairly stable to further hydrolysis and solution chemistry, resulting in higher coagulation efficiency. The fraction of Al that does not react with the Ferron reagent within the time of
experiment (typically 120 min), i.e. a non-reactive fraction (Alc), is assumed to represent colloidal, solid-phase or polymeric Al (Okura 1962). A slightly modified method was used here. The ferron reagent used by some previous researchers exhibited some unstable features. A continuous change in the absorption spectrum of the colorimetric reagent with aging was observed. Therefore, it has been suggested that determination of total dissolved aluminum and polymeric aluminum by use Erichrome cyanine R dye with indirect calorimetric analysis, in which the absorbance at wavelength of 353 nm is related to the concentration of reactive aluminum. The complex compound formed between $\text{Al}^{3+}$ and Erichrome cyanine R has an absorption peak at 353 nm. The time dependence of the reaction between aluminum species and Erichrome cyanine R has been described as the pseudo first-order rate constant $k$ for specie Alb (polymer) (Kerven et al, 1989).

**XRD Test for characterization PACs**

The powder samples of PAC and PAC–Al$_{13}$, dried in a vacuum oven, were analyzed using BRUKER, Germany model D8 ADVANCED with a Cu Kα source ($\lambda$=1.54 Å) and random packed powder diffraction mounts. Samples were scanned from 5 –70° 2θ.

**RESULTS AND DISCUSSION**

**Optimum conditions for alumina extraction**

**Effect of acid concentration**

To investigate the effect of acid concentration the series of experiments were performed at 90 °C for 2 hours. This series were studied on calcined (650 °C) and uncalcined -200 mesh samples of kaolin by using different acid concentrations (2, 5, 8 N) at acid/clay ratio 10:1 w/w. The obtained results are shown in Fig.5, which reveal that the alumina extraction is increased by increasing acid concentration and it is also noticed that the extraction extent is increased by calcination from 17.84 % to 50.81 % at 8N.

![Figure 5. Effect of acid concentration](image)

**Effect of temperature**

To investigate the effect of temperature on the leaching process on the extent of alumina extraction from -200 mesh clay, a series of experiments were carried out at 8N acid concentration for 2 hours at fixed acid/clay ratio of 10:1 w/w and the temperature varies from 50- 90 °C on calcined (650 °C) and uncalcined clay. The results in Fig. 6 show that the extent samples of aluminum extraction is sharply increased by increasing the leaching temperature . Also the percent of extraction is highly raised from 17.84 % to 50.7 % by using the uncalcined samples and calcined samples (650 °C), respectively.

**Effect of leaching time**
To investigate the effect of time of leaching process on the percent of alumina extraction from -200 mesh, a series of experiments were performed at 90 °C by using 8N acid concentration. This series were studied for different times ranging from 2-12 hours at calcined (650 °C) and uncalkined samples.

![Figure 6. Effect of temperature](image)

Figure 6 shows a slight increase in the percentage of extracted aluminum oxide from clay by increasing the leaching time. It is also noticed that, calcination(650 °C) raises the extraction extent from 29.8% to 65.6% after a leaching time of 12 hours.

**Effect of acid/clay ratio**

To investigate the effect of acid/clay ratio, a series of experiments were carried out at 90 °C for 12 hours by using 8 N acid concentration. Acid/clay (wt/wt) was changed from 6:1 to 14:1 for calcined and uncalkined samples. The results in Fig. 7 reveal that, the extraction of alumina is increased by increasing the acid/clay ratio reaching its maximum value of 30.16% and 65.8% for uncalkined and calcined samples, respectively, at the ratio of 10:1; there is no noticeable increase in the extraction of alumina with further increase on acid/clay ratio more than 10:1(w/w).
Effect of calcination temperature on the percent of extracted alumina (overall optimum conditions)

To investigate the effect of calcination temperature of leaching process on the yield of alumina extracted from -200 mesh clay. A series of experiments were performed at different calcination temperatures from 500 to 700 °C for 2 hours and the leaching experiments were carried out at 90 °C for 12 hours using 8 N and acid/clay ratio 10:1 (w/w). The results in Fig.9 reveal that the alumina extraction increases from 69.4% at 500 °C to 77.29% at 650 °C after that there is no pronounced increase. Therefore, calcination temperature of 650 °C is considered as the optimum calcination temperature.
The kinetic absorbance of PACs with various basicities are shown in Figs. 10 and 11. A complete set of information can be found in Table 1. The shapes of the Al-kinetic curves are similar, whether the PACs were prepared from pure aluminum chloride or aluminum chloride extracted from Egyptian kaolin. All curves rise sharply in the first 60 min then slow show a increase and become almost flat in the last 60 min. The polymeric aluminum \((Al_{13})\) increases with increasing the basicity ratio(OH/Al. So PAC \((n=2.2)\) has more polymeric aluminum \((Al_{13})\) than that PAC \((n = 2,1.5\) and 1). It is noticed also that , the percent of polymeric aluminum has reached to 82.94% at \(n = 2.2\) for PAC from pure aluminum chloride which is 80.77% at \(n = 2.2\) for PAC from aluminium chloride from kaolin ; which reveals that they are nearly the same value . So we consider that PAC prepared from pure aluminium has the same characteristics as that prepared from kaolinite.
Figure 11. Absorbance vs. time for PACs (0.1M [Al]) prepared from pure aluminum chloride.

Figure 12. XRD spectrum for aluminum chloride extracted from Egyptian kaolin.
3.2.2 XRD The Al$_{13}$ signals appeared in the range of 2θ from 5° to 25° in XRD spectrum (Wang, 1999). Also various peaks can be observed, indicating initially a crystalline character of PACs. Specifically, the intense peaks at 27°, 32°, 46° and 57°, and 67° are attributed to the unavoidable by-product, formed during the neutralization of the Al solution with the NaOH solution during the preparation of coagulants. Presence of NaCl, which is an Figs. 12 and 13 are the X-Ray diffraction patterns for aluminum chloride produced from kaolin sample and pure aluminum chloride. Both Figs show that there is no difference between both patterns and spectra (card 44 – 1473, 77- 1884 and 77- 0819). Figs. 14 and 15 are the X-ray diffraction spectra for PAC produced from pure aluminium chloride and that from kaolinite respectively at n = 1, 1.5, 2 and 2.2. It is noticed also that, using aluminum chloride which is produced from kaolinite samples has no bad effect on the final PACs product.
Figure 13. XRD spectrum for pure Aluminum chloride

(a)
PAC from pure AC

n = 1.5
PAC from pure AC

n = 2.2
Figure 14. (a), (b), (c) and (d) are XRD spectra for PACs prepared from pure aluminum chloride.
PAC from Kaolinitic AC

n = 1
PAC from Kaolinitic AC

n = 1.5
PAC from Kaolinitic AC

n = 2.2
Figure 15. (a),(b),(c) and (d) are XRD spectra for PAC₅ Prepared from aluminum chloride extracted from Egyptian kaolin.
Application of the prepared poly aluminum chloride
Removal of turbidity

Actual surface water with turbidity of 8.16 NTU and pH of 8.14 was taken from River Nile, Egypt and used for jar test. The coagulants alum, AlCl₃, PAC and PAC–Al₁₃ were selected to compare their turbidity removal efficiency. The results are shown in Figs. 16 and 17. It can be seen that PAC–Al₁₃ and PAC performed much better turbidity removal than alum and aluminum chloride. During the experiment, it was also found that the flocs formed by PAC–Al₁₃ are larger than those formed by alum, aluminum chloride and PAC. The results show also that PAC–Al₁₃ possesses stronger charge-neutralization characteristics than alum, AlCl₃ and PAC, because good turbidity removal occurs when flocs of mud possess a negative charge. This suggests that both PAC–Al₁₃ and PAC perform coagulation/flocculation by charge-neutralization and the bridge-formation mechanism.

Natural organic matter removal

Natural organic matter (NOM) in Nile river is a complex mixture of molecules with varying molecular weight (MW) and chemical nature. It can cause odor, taste, color and bacterial re-growth in potable water. Even worse, it is a precursor for disinfection by-products, such as trihalomethanes (THMs) and haloacetic acids (HAAs), which has proven to be carcinogens. Thus, effective removal of NOM is a major objective of modern drinking water treatment. At present, coagulation and flocculation is the most common process used for the removal of NOM in water treatment. Polyaluminum chloride (PAC) is used as the coagulant, which has replaced many traditional aluminos coagulants in recent years. Previous studies have shown that Al (III) species in PAC can be driven into various hydrolyzed Al species such as monomeric and dimmeric Al species [Al(OH)³⁺, Al(OH)²⁺ and Al(OH)₁⁺, Al₂(OH)₂⁴⁺, denoted as Al₁₃, tridecamer [Al₁₃O₄(OH)₂₄]¹⁷⁺, Al₁₃ for short] and other unknown species including amorphous precipitate Al(OH)₃(am). Fig. 18 show NOM removal by the four kinds of Al coagulants in the dose range of 10 – 25 mg/l. TOC were estimated by Phoenix 8000 UV persulfate analyzer and the results show that PAC–Al₁₃ which contain Al₁₃ species give the most effective particle removal, which was due to Al₁₃ species have higher charge neutralization ability. So the charge neutralization played an important role in the coagulation at low doses.
Figure 17. Turbidity removal via PACs prepared from extracted aluminum chloride from kaolin

Figure 18. TOC removal via PACs prepared from pure aluminium chloride
Figure 19. TOC removal via PACs prepared from extracted aluminum chloride from kaolin

Figure 20. Change in pH by use PACs prepared from pure AC
Change in pH by different coagulants

The pH of raw water gives an indication of how acidic or alkaline is. It is a very important parameter in water treatment, especially for effective coagulation. Each coagulant has a narrow optimum operating pH range. If the pH is lower or higher than this optimum, then problems of high residual color or aluminium shall occur. The river Nile pH was 8.14 and the different four types of coagulants are represented in Fig. 20 and 21. The results revealed that the pH of tested water is slightly affected with alum and PACs while it show pronounced decrease by using aluminum chloride, so the PAC has no effect on water pH.

CONCLUSION AND SUGGESTIONS

The optimum conditions for extraction of alumina (78%) from Egyptian kaolinitic clay are particle size -200 particle size, calcined at 650 °C for 2 hours, treated with 8 N acid concentration, at 90 °C for 12 hours and acid to clay ratio 10:1.

The fraction of polymeric Al reached a maximum \(\text{Al}_{13}[\text{Al}_{13}\text{O}_4\text{(OH)}_{24}]^{7+}\) at \(n = 2.2\) about 82 % of the total aluminum[0.1 M] in solution.

The coagulation tests for the synthesized PACs showed that the PAC (\(n = 2.2\)) coagulant is the most efficient for TOC and turbidity removal among the coagulants used due to its highest amount of polymeric Al species \(\text{Al}_{13}[(\text{AlO}_4\text{Al}_{12}\text{(OH)}_{24}(\text{H}_2\text{O})_{12})^{7+}]\) contained in the PACI (\(n = 2.2\)). Optimum dose for river Nile turbidity removal (8.16 NTU) was 10 mg/l from PAC\((n=2.2)\) which shows better results than 25 mg/l from alum.

The PACs-\(\text{Al}_{13}\) is more effective in turbidity removal than commercial PAC.

PAC does not change the pH degree of water as traditional coagulants (aluminum chloride).

The PACs coagulation test on Nile river waters with, PACs \([n = 1.0, 1.5, 2, 2.2]\), showed that the efficiency of coagulation is in the order, \((n = 2.2 >2 >1.5 >1)\) corresponding to the order of polymeric aluminum contents. The results above confirm that the \(\text{Al}_{13}[(\text{AlO}_4\text{Al}_{12}\text{(OH)}_{24}(\text{H}_2\text{O})_{12})^{7+}]\) species has a higher positive charge and is the most effective polymeric Al species for surface water treatment, and that both PAC–\(\text{Al}_{13}\) and PAC achieve more coagulation/flocculation than alum and aluminum chloride.

![Figure 21. change in pH by use PACs prepared from extracted aluminium chloride](image)

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