REMOVAL OF SOME POLLUTANTS BY POLY INORGANIC COAGULANTS BASED ON SILICA DERIVED FROM RICE HUSK ASH

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Abstract:

Coagulation is one of the most important steps during the conventional water treatment train . Salts and prehydrolysed salts of aluminum and iron were used as coagulants in water and waste water treatment; These effective materials play a vital role in the removal of a board range of impurities from water including colloidal particles, dissolved organic substances and some heavy metals.

Because of superior efficiency and relatively low cost of these materials compared with traditional coagulant alum, aluminum salts and iron salted of the prehydrolysed iron and aluminum salts with active silica were favorable in addition to the following features: very fast hydrolysis , promote rapid settling rates, extremely efficient in cold water, give low soluble residual aluminum, consume less alkalinity, very little effect on pH, increase stability of coagulant and denser compacted sludge.

The objective of this study is to prepare four new types of poly inorganic co-agulants (PIC); these are poly aluminum chloride silicate (PACISi), poly hydroxy aluminum sulphate silicate (PHASSi), poly ferric chloride silicate (PFeClSi), and poly ferric aluminum chloride silicate (PFeAlClSi) based on silica. The characterization of the materials obtained was carried out by means of by FTIR, NFTIR, XRD, and SEM., in order to select the optimum condition suitable for removal of some pollutants. Under this study the maximum removal of some ground water pollutants as turbidity , colour, Fe, Mn, Pb, As, NO_3^{-1} and F^{-1} are about 70%,75% 97.5%, 96%, 97%, 97%, 97%, and 99% respectively ; the maximum removal of Pb in industrial waste water reach to 99%; the maximum removal of BOD, COD and TSS in sewage waste water are 92 %, 90 %, 93 % , respectively .

KEY WORDS : Inorganic coagulants. silica based coagulants and Waste water Treatment.

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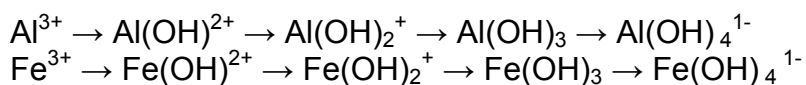[3] Atomic Energy Authority, Egypt
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INTRODUCTION

Aluminum and ferric salts are widely used as coagulants in water and wastewater treatment. These materials have been applied routinely since early in the 20th century and play a vital role in the removal of many impurities from polluted waters. They are effective in removing a broad range of impurities from water, including colloidal particles , dissolved organic substances and dissolved constituents from water beside arsenic, notably turbidity, iron, manganese, phosphate, fluoride . Their mode of action is broadly understood Charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous precipitate of metal hydroxide. The relative importance of these two mechanisms depends on many factors, especially pH and coagulant dosage[1].

All ions in water are hydrated to some extent. In the case of Al^{3+} and Fe^{3+}, there is a primary hydration shell with six octahedrally coordinated water molecules, e.g., $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$. Hydrolysis of such ions is often represented as a sequential replacement of the water molecules by hydroxyl ions, and can also be thought of as a progressive deprotonation of water molecules in the primary hydration shell, the hydrolysis of aluminum salt could produce a series of products ranging from monomers, oligomers to polymeric hydroxyl complexes. Most of them, such as, $Al(OH)_{3(am)}$ $Al(OH)_2^+$, $Al(OH)^{2+}$, Al^{3+} ,$Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}^{7+}$ (tridecameric polymer or 'Al$_{13}$'), [2] the simplest representation, for Al^{3+}, and Fe^{3+} omitting the hydration shell for convenience, is:

$$Al^{3+} \rightarrow Al(OH)^{2+} \rightarrow Al(OH)_2^+ \rightarrow Al(OH)_3 \rightarrow Al(OH)_4^{1-}$$
$$Fe^{3+} \rightarrow Fe(OH)^{2+} \rightarrow Fe(OH)_2^+ \rightarrow Fe(OH)_3 \rightarrow Fe(OH)_4^{1-}$$

Since each step involves the loss of a proton, increasing pH causes the equilibrium to be shifted to the right. Aluminum hydroxide has low solubility in water, and precipitation occurs at intermediate pH values. Further increase of pH causes the soluble aluminate ion to be formed. A similar sequence can be written in the case of Fe^{3+}. In this case, the hydroxide is much less soluble than aluminum hydroxide[2].

Coagulants are one of the key factors in the coagulation process. Alum is the most frequently applied traditional coagulant in the world. Recently, based on conventional iron and aluminum salts, inorganic polymer flocculants (IPFs) have been developed rapidly and become applied widely, especially in China, Japan, Russia, and west Europe [3-6]. Many kinds of IPFs have been developed including aluminum-based, iron-based, inorganic–inorganic composite flocculants, inorganic–organic composite flocculants, and multifunctional composite IPFs [3-9]. A number of experimental methods and approaches have been applied. Apart from normal chemical analysis, the analytical methods applied were potential titration, small angle X-ray diffraction, infrared spectroscopy, nuclear magnetic resonance spectroscopy, laser light scattering, small angle X-ray scattering, various electron microscopy, and atomic force microscopy. The timed spectrophotometer method involving reaction of 8-hydroxyquinoline or ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid) has also been widely applied to quantify the different species present[10-18].

In water treatment, the pre-polymerized aluminium salts offer a number of potential benefits in comparison to the precursor Al salts. These benefits were noted to varying degrees depending on the characteristic properties of the raw water; improved performances in the overall coagulation-flocculation- sedimentation processes' improved performances in conditions which often limit the rate and extent

of hydrolysis and coagulation, e.g. low pH, low alkalinity, presence of organic contaminants , and low temperatures, reduced levels of residual soluble Al species, reduced requirements for organic polymer flocculants and lower pre- or post flocculation pH adjustments needed [19,20].

Aluminum salts and activated silica, a sort of polysilicate (PSi), can be combined under some conditions to prepare PASiC coagulant. They may be prepolymerized by hydroxylation individually or mixed initially in their original form and then hydrolyzed together[21-22], some studies demonstrated that adding Al or other salts can delay the gelation time of activated silica Also, there are several reports indicating that aluminum-silicate polymer composites are highly effective for removal of turbidity and humics and for treatment of cold water [23-24].

The IPFs, such as poly aluminium chloride (PACl) and poly iron chloride (PICl), are a category of partially neutralized metal salts with significant polymeric fraction present in some circumstances. Preformed polymerized species have the advantages of being more effective under a variety of water quality conditions, especially at lower temperatures and a broader pH ranges relative to alum [25–27].

Previous studies paid most attention to the effect of alkalinity on the coagulation behaviors of traditional coagulants, and little study has been focused on the effect of alkalinity on coagulation with PACls, It has been observed that demand for alum increases linearly with increased alkalinity and turbidity is hard to remove when alkalinity drops below 30 mg/L as CaCO$_3$,Alkalinity also plays a key role in the enhanced coagulation to remove NOM, since it tends to keep coagulation pH higher and reduce NOM removal . PACls could be less affected by alkalinity than alum, particularly those PACls with higher basicity [28-29].

The general mechanisms of coagulation have been summarized in Duan and Gregory's review in detail [30]. Colloidal destabilization can be achieved by adding alum, and the corresponding mechanism involved is called charge neutralization. Due to the extremely low solubility of aluminum, with increase of alum dosage, rapid and excessive aluminum hydroxide precipitation can form and fine particles in water can be enmeshed in the hydroxide precipitate, and thus efficient turbidity removal is achieved. This process is the so-called sweep flocculation mechanism since particles are swept out of water by an amorphous hydroxide precipitate. Chowdhury and Amy [31]. claimed that precipitation is the main mechanism in the coagulation of alumina colloids with alum. According to the 'sweep flocculation' model, the incorporation of colloids into precipitate follows two pathways: one is the heterogeneous nucleation involving charge neutralization and subsequent growth of precipitate at low pH values, and the other is homogeneous nucleation involving precipitation and subsequent particle aggregation at high pH values. In this study, the former pathway is regarded as charge neutralization and the latter one as sweep flocculation. With respect to the coagulation/flocculation mechanisms of PACls, most current studies focused on the mode of charge neutralization [32-33]. tried to explain the coagulation mechanisms of different kinds of coagulants by a combined model of precipitation charge neutralization (PCN). Recently, 'electrostatic patch coagulation' (EPC) was proposed by Wang et al. [34].

The objective of this study is to prepare four new types of poly inorganic co-agulants (PIC); these are poly aluminum chloride silicate (PAClSi).,poly hydroxy aluminum sulphate silicate (PHASSi.) poly ferric chloride silicate (PFeClSi),poly ferric aluminum chloride silicate (PFeAlClSi) based on silica. The characterization of the materials

obtained was carried out by means of by FTIR, NFTIR, XRD, and SEM. in order to select the optimum condition suitable for removal of some pollutants.

2. Materials and Experimental procedure

2.1. Materials

All reagents(aluminum chloride, ferric chloride, aluminum sulphate, sodium carbonate) used are analytically pure chemicals except sodium silicate which is a commercial grade product prepared from RHA and pure sodium hydroxide .Deionized water was used to make all solutions.

2.2. Experimental

The experimental part is divided into two main sections:

(i) The first section is subdivided into two parts:

the first part concerns with preparation of poly silicic acid solution (PSi) from sodium silicate based on RHA was chosen as a precursor for the preparation, by dilution of sodium silicate containing 15 % SiO_2 with distilled water to a concentration of 0.25 M SiO_2 . The diluted solution was reacted with 0.25 HCl under magnetic stirring, the pH of final solution about 2 and SiO_2 concentration reaches 0.125 M, the second part concerns with the preparation and characterization of a new four poly inorganic coagulants namely poly aluminum chloride silicate (PAClSi), poly hydroxy aluminum sulphate silicate (PHASSi.) poly ferric chloride silicate (PFeClSi), poly ferric aluminum chloride silicate (PFeAlClSi) .The preparation was done by the slight neutralization of inorganic coagulant (0.25M $AlCl_3$, 0.125M $Al_2(SO_4)_3$, 0.25M $FeCl_3$, and (0.25M $ALCl_3$ or $FeCl_3$) with sodium carbonate 0.25 M at 60 °C with rapid mixing to obtain [γ= 2, в= 67, r_1=0.1], [γ =1.5, в =50% r_1=0.1]. [γ= 2, в= 67%, r_2 =0.2], and [γ= 2, в= 67 %,- r_1= 0.1 r_2 =0.2] respectively where γ is the molar ratio of [OH]/[AL] , в represents the basicity , the r_1 is the molar ratio of aluminum to silicon and r_2 is the molar ratio of iron to silicon .

(ii) The second section is subdivided into three main parts:

the first part concerns with the removal of some pollutants from ground water such as iron ,manganese , arsenic, lead , fluoride, and nitrate ions in addition to turbidity and colour using representative sample obtained from a certain well. The second part concerns with the removal lead from industrial waste water. The third part concerns with removal of BOD, COD and TSS from sewage waste water to obtain the water quality for re-use in agricultural drip irrigation system. Whereas, the treatment is depended on precipitation ,coagulation and adsorption technique using poly inorganic coagulants(PIC), Each sample was mixed with 5-10 ppm of PIC and agitated for 1minute rapid mix (300rpm), 5 minutes slow mix (30rpm), 20 minutes (standing time The concentration was measured in the filtrate using AAS and normal analytical methods according to ASTM.

3. Results and discussions

3.1. The first section:

The data listed in Table (1) represent the chemical composition of four samples of poly inorganic coagulants, namely, poly aluminium chloride silicate (PACISi), poly hydroxy aluminium sulphate silicate (PHASSi.) poly ferric chloride silicate (PFeCISi),poly ferric aluminium chloride silicate (PFeAlClSi)Fig.1a shows the FTIR spectrum of poly aluminium hydroxy sulphate silicate (PAHSSi), the spectrum displayed the characteristic bands of OH – stretch, H_2O bend, AL-OH_2 bend, Si-O stretching SiO$(OH)_3$, Al-O symmetric stretch SO_4 ,and or Al-O-Si, symmetrical and anti-symmetrical ALO_4 at 3372, 1671, 1135 cm^{-1} , 606, and 505 cm^{-1}, respectively [35-36] . Fig.1b) shows the FTIR spectrum of poly aluminium chloride silicate (PACSi), the spectrum displayed the characteristic bands for Si-OH stretching, OH – stretch, H_2O bend, AL-OH_2 bend , Si-O stretching SiO$(OH)_3$, Al-O symmetric stretch ,and or Al-O-Si symmetrical and anti-symmetrical ALO_4^{-1} at 3735, 3435 , 1636, 1086, 983 and, (598,422) cm^{-1}, respectively [35-36]. Fig.1c shows the FTIR spectrum of poly ferric chloride silicate (PFeCISi), the spectrum displayed the characteristic bands of Si-OH stretching ,OH – stretch, H_2O bend Fe-OH_2 bend , Si-O stretching SiO$(OH)_3$, Fe-O symmetric stretch , Fe-O-Si or symmetrical and anti-symmetrical FeO_4^{-1} at 3876, 3383, 1619 , 1082, 958, 689, and, (465,417) cm^{-1} respectively [35-36] Fig.1d) shows the FTIR spectrum of poly aluminum ferric chloride silicate PAlFeCLSi, the spectrum displayed the characteristic bands for OH – stretch, H_2O-OH stretch, H_2O bend AL-OH_2 bend , Si-O stretching SiO$(OH)_3$, Al-O symmetric ,and or Al-O-Si and anti-symmetrical ALO_4^{-1} (FeO_4^{-1}) at 3413 , 1629 , 1121, 898 , 702, and 480 cm^{-1}respectively,[35-36].

Fig.2a shows NFTIR spectrum of Poly aluminium chloride silicate (PACSi), the spectrum displayed the characteristic bands of overtone OH – stretch Si-OH, overtone OH - stretch(1)AlOH, combination of (OH-stretching(1+2) AlOH+ crystal water ,overtone OH-stretching AlOH vicinity $AlOH_4$, H_2O combination (bend 1 + stretch 1) Al_{13}) ,H_2O combination (bend 2 + stretch 1) crystal H_2O +Al_{13}) and combination AlOH (stretch 1 + bend 3 or 4) at 7326 (7040 ,6984 and 6914) ,(6823-6787), 5436 , 5341, 5181, and 4463cm^{-1} respectively[36-37]. Fig.2b shows NFTIR spectrum of Poly aluminium hydroxy sulphate silicate (PAHSSi) , the spectrum displayed the characteristic bands of overtone OH – stretch Si-OH ,overtone OH - stretch , (1) AlOH ,combination of (OH-stretching(1+2) AlOH+ crystal water overtone OH-stretch (2) H_2O, overtone OH-stretching AlOH vicinity $AlOH_4$, H_2O combination (bend 1 + stretch 1) Al_{13}) ,H_2O combination (bend 2 + stretch 1) crystal H_2O +Al_{13}) at 7336 ,(7020, 6982 and 6914) ,(6871 , 5436c, 5341) and 5177cm^{-1} respectively[36-37]. Fig.2c shows NFTIR spectrum of poly ferric chloride (PFeCISi) ,the spectrum displayed the characteristic bands for overtone OH – stretch Si-OH ,overtone OH – stretch, (1) FeOH, combination of (OH-stretching(1+2) FeOH+ crystal water, overtone OH-stretch (2) crystal H_2O, (overtone FeOH (3/4) bend, overtone OH-stretch FeOH vicinity $FeOH_4$) , H_2O combination (bend 2 + stretch 1) crystal H_2O +Al_{13})and combination H2O (bend 2 + stretch 2) crystal H_2O combination FeOH at 7378 , (6898) ,(6813 and 6732) and 6600-6060 ,5880 and 5513 , 5138 ,4565 cm^{-1} respectively [36-37] fig.2d shows NFTIR spectrum of Poly aluminium ferric chloride silicate (PAlFeCSi),the spectrum displayed the characteristic bands of overtone OH – stretch Si-OH, overtone OH – stretch, (1) FeOH/AlOH combination of (OH-stretching(1+2) FeOH or AlOH +

crystal water, H$_2$O combination (bend 1 + stretch 1) Al$_{13}$) combination (bend 2 + stretch 1) crystal H$_2$O +Al$_{13}$) or at (7368,7326)7040, (6802- 6743), (6446-6366), and 5199 cm^{-1} respectively [36-37]:FTIR and NFTIR were summarized in table 2 &3.

Fig.(3) shows SEM micrograph of PACSi -C$_2$O$_4$ which indicates the hexagonal crystalline form; Fig.(4) shows the SEM micrograph of PACSi-SO$_4$ which identifies by the fiber shaped and monoclinic rectangle crystalline form, Fig.(5) shows SEM micrograph of PAHSSi which indicates the mono clinic rectangle crystalline form; fig.(6) shows SEM the scan electron microscope of PFeClSi which identifies by the spherical form with aggregates and Fig.(7) shows SEM micrograph of PFeAlClSi which identifies by the spherical form with aggregates.

Fig. (8) shows the X-ray diffractogram of poly aluminum chloride silicate (PACSi), which indicates the silica abroad peak appeared around 2θ equal to 22°[38], high intensity and sharp peaks in the range of 2θ from 5 to 25°[38], which indicates that there is Al$_{13}$ species in PAC–Al$_{13}$ [38]; Fig. (9) shows the X-ray diffractogram of poly aluminum hydroxy sulphate silicate (PAHSSi), which indicates the amorphous silica appeared abroad peak around 2θ equal to 22°, peaks in the range of 2θ from 5 to 25°[38], which indicates that there is Al$_{13}$ species in PAC–Al$_{13}$ and amorphous sulphate [38], Fig. (10) shows the X-ray diffractogram of poly ferric chloride silicate (PFeCSi), which indicates the amorphous silica board peak appeared around 2θ equal to 22°[38] and the peak in the range of 2θ equal to 32° and Fig. (11) shows the X-ray diffractogram of poly ferric aluminum chloride silicate (PFeACSi),which indicates the amorphous silica board peak appeared around 2θ equal to 22° [38],and the peak in the range of 2θ equal to 32°.

3.2. The second part :

The data listed in table (4) represents the variation of physicochemical properties of ground water with four samples of poly inorganic coagulant silica based , it was shown that : the maximum removal of iron, manganese colour, and turbidity, reach to 97 %, 25%, 73%, 74%, in case of PACSi, PACSi PAHSi, and PAlFeCl, respectively, The data listed in table (5) represents the variation of physicochemical properties of alkaline ground water by inorganic polymers; it shown that, the maximum removal of iron, manganese, fluoride, reach to 99 %, 97%, 99%, in case of PFeAlClSi, The data listed in table (6) represents the variation of physicochemical properties of alkaline ground water sample spiked with some pollutants; the maximum removal of color, turbidity , Iron , manganese, arsenic, lead, nitrate and fluoride, reach to 67%, 86%, 99 %, 57%, 97%, 98%, 79 % and 19% respectively, in case of PFeAlClSi. In all cases the residual aluminium not more than permissible limits 0.2 mg/l, bicarbonate decrease by addition of coagulant due to consumption of alkali by slightly acidic poly inorganic coagulant , concentration of sulphate and chloride increase by using poly inorganic coagulant , concentration of sodium increase due to using sodium carbonate to raise pH, concentration of total dissolved solids and electrical conductivity increased due to spiking of new materials in solution, no considerable variation of calcium, magnesium, potassium, nitrite, phosphate and silicate. In table 7 the treatment of sewage waste water by poly inorganic polymers based on silica showed that, the maximum removal of BOD$_5$, COD and TSS reach to 92 %, 90%, 93%,respectively, with poly ferric aluminum chloride silicate, total dissolved solids increases due to a new spiked ions , no

variation of pH occurred, all values after treatment within permissible limits according to Egyptian low 44/2000 . From table 8 the treatment of industrial waste water by poly inorganic polymers showed that, the maximum removal of Lead reach to 99%,in case of PAHSSi .

3.3. the proposed mechanisms

Coagulants destabilize colloids and heavy metals by a combination of four mechanisms; these based on compression of the double layer, counter ion adsorption and charge neutralization, enmeshment in a precipitate, and heterocoagulation.[40, 41]

1. Compression of the Double Layer (DLVO Theory)

As the concentration of counter ions in solution increases, the counter ions leads to the neutralization of the net charge in the diffused layer and resulted in the compression of this layer. This compression affects the thickness of the entire double layer and so allows colloids to come closer together.

2. Counter ions adsorption and charge neutralization

Counter ions of coagulants can also be adsorbed onto the surface of the colloidal particles. In this way, the repulsive charges on the surface of the particles may be fully neutralized by the charges carried by the counter ions.

3. Enmeshment in a precipitate

The dosage of metal salts used in coagulation is usually slightly in excess of the amount required for reduction of the zeta potential. The excess metal salts hydrolyze into the form $M(OH)_6^{3+}$. These hydroxides are extremely insoluble in water. As the hydroxide precipitate forms and accumulates; the small colloidal particles are entrapped or enmeshed in the hydroxide floc structure ("enmeshment in a precipitate"; "sweep-floc coagulation").

4. Heterocoagulation

The surface charge on the surface of some naturally occurring particles may not be uniform. Oppositely charged sites may exist on the surface of the same particle. The coagulation of these colloidal particles can therefore occur via simple electrostatic interaction between these oppositely charged sites ("heterocoagulation").

Most particles in water, mineral and organic, have electrically charged surfaces, and the sign of the charge is usually negative [41] ,in activated silica case, two important processes for producing this charge are considered in the following discussion:

First, surface groups on the solid may react with water and accept or donate protons. For an oxide surface such as silica, the surface site might be indicated by the symbol SiOH and the surface site ionization reactions take place:

$SiOH_2^+ \longrightarrow SiOH + H^+$
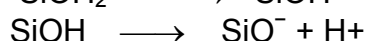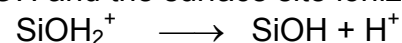
$SiOH \longrightarrow SiO^- + H+$

Second, surface groups can react in water with solutes other than protons. Again, using the SiOH surface groups of silica,

$SiOH + M^{2+} \longrightarrow SiO M^+ + H^+$ where, M= Fe, Mn, As, and Pb

$SiOH + Mo^{2-} \longrightarrow SiOPO^3 H^- + OH^-$ where, MO^{2-} = $2F^{-1}$, $2NO3^{-1}$,and HPO_4^{2-}
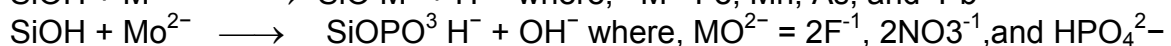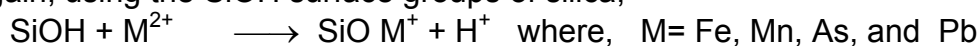
These surface complex formation reactions involve specific chemical reactions

between chemical groups on the solid surface (e.g., silanol groups) and absorbable solutes (e.g., Lead and Nitrate ions). Surface charge is again related to solution chemistry [41].

4. CONCLUSIONS

Within limits of the present study the following conclusion can be derived :

1) Sodium silicate (activated silica) was regarded as   one of coagulant modifiers which has many features like very fast hydrolysis , promote rapid settling rates, extremely efficient in cold water, give low soluble residual aluminum, consume less alkalinity, very little effect on pH, increase the stability of coagulant and leads to a denser compacted sludge.

2) Poly inorganic coagulant based on silica of iron are more favorable than aluminium due to a broad range and highly density of iron hydroxide than aluminum hydroxide.

3) Mixtures of aluminum and iron poly co-agulants are more efficient in removal of pollutants of waste waters.

4) Maximum removal of ground water pollutants : turbidity , colour, Fe, Mn, Pb, As, NO_3^{-1} and F^{-1} are found to be about 70%,75% 97.5%, 96%, 97%, 97%, 97%, and 99%, respectively ,

5) The maximum removal of Pb in industrial waste water reach to 99%,

6) The maximum removal of BOD, COD and TSS in sewage waste water are found to be 92 %, , 90%, and 93%,respectively.

7) The maximum doses in all cases about 10 ppm of Fe and Al coagulant based on activated silica .

8) The residual aluminium level does not exceed the permissible limits 0.2 mg/l .

Table(1): Chemical composition of poly inorganic co-agulants with silica

Parameter	PACSi	PFeClSi	PAHSSi	PAlFeClSi
Al g/l	3.5	-	3.5	1.75
F g/l	-	10	-	5
Si g/l	0.35	1	0.35	1
β	66 %	66 %	50 %	66 %
γ	2.0	2.0	1.5	2.0

Fig(2) : Band components analysis of the infrared spectra (cm^{-1})
of poly inorganic coagulants based on silica

Al$_{13}$.-O-Si(OH)$_3$[36]	PACSi	PFeClSi	PAlHSSi	PAlFeClSi	Assignment
3740	3735	3876			Si-OH OH-stretch
3449–3465	34345	3383	3372		OH-stretch (1)
3163– 3245				3413	H$_2$O OH-stretch (2)
1680-1618	1636	1619	1671	1629	H$_2$O bend (1), H$_2$O bend (2)
1164 1076	1086	1082	1135	1121	Al-OH$_2$ /Fe-OH$_2$bend (1), v$_3$ SO$_4$ or v$_1$ SO$_4$ /Al-OH$_2$/Fe-O bend (2)
984	983	958		898	Al-OH$_2$ / Fe-OH$_2$ bend (4)
683– 706	600	689		703	Al-O / Fe-O antisymmetric stretch or Al-O / Fe-O symmetric stretch AL-O-Si / Fe-O-Si
593– 606			606		v$_4$ SO$_4$

Fig(3) :Band components analysis of the near infrared spectra(cm^{-1})
of poly inorganic coagulants based on silica

PAC Al$_{13}$SO$_4$ [39]	PACSi	PAHSSi	PFeClSi	PAlFeClSi	Assignment
	7326	7336	7378	7368,7326	Overtone OH-stretch Si-OH
7018	7040 , 6984	7020 , 6982-6914	6898	7040	Overtone OH-stretch (1) AlOH or FeOH
6777	6787-6823	6871	6813	6802 - 6743	Combination OH-stretch (1 + 2) AlOH + crystal H$_2$O or FeOH
6213	-	-	6248	6446-6366	Overtone OH-stretch (2) crystal H$_2$Oor FeOH
5703	5436	5436	5778	5199	Overtone AlOH(3/4) bend or FeOH
5236	5341	5341	5513	-	**H$_2$O combination (bend 1 + stretch 1) Al$_{13 , or}$ FeOH**
5158	5181	5177	5138	-	H$_2$O combination (bend 2 + stretch 1) crystal H$_2$O+ Al$_{13,}$ or FeOH
4553	4463	-	4565	-	Combination AlOH (stretch 1 + bend 3 or 4) or FeOH

Table(4):Variations of physicochemical parameters of ground water samples by influence of poly inorganic co-agulants based on silica

		Coagulants / Parameters	G.W	PACSi	PAHSSi	PFeClSi	PAlFeClSi	Permissible Limits
PHYSICAL PARAMETERS		colour mg/l	35	12	11	28	12	< 20
		TDS mg/l	552	625	566	662	638	< 1200
		Turbidity NTU	8.9	2.5	2.3	2.5	2.3	< 5
		EC μmohs/cm	861	1005	904	1066	1028	< 1200
CHMICAL PARAMETERS		PH	7.40	7.59	7.13	7.11	7.39	6.5-9.2
	MAJOR ANIONS	CO_3^{--} mg/l	0.0	0.0	0.0	0.0	0.0	-
		HCO_3^{-} mg/l	307	270	202	242	260	-
		Cl^{-} mg/l	62	117	60	157	120	< 500
		SO_4^{--} mg/l	59	65	149	70	70	< 400
	MAJOR CATIONS	Na^{+} mg/l	36	70	51	80	72	< 200
		K^{+} mg/l	4	4.0	4.0	4.0	4	< 10
		Ca^{++} mg/l	90	82	82	81	42	< 200
		Mg^{++} mg/l	31	30.0	30.0	29.4	30	< 150
	NUTRIENT SALTS	NO_2^{-} μg/l	0.001	0.003	0.004	0.002	0.005	< 0.005
		NO_3^{-} μg/l	0.030	0.010	0.053	0.094	0.122	< 10
		NH_3 mg/l	0.05	0.03	0.04	0.03	0.02	-
		SiO_2 mg/l	29.00	25.20	25.00	29.40	32.10	-
		TP μg/l	0.822	1.033	0.861	1.039	1.06	-
	Heavy metals	Fe mg/l	1.946	0.059	0.185	0.701	0.284	< 1.0
		Mn mg/l	2.1	1.64	1.67	1.95	1.95	< 0.5
		Al mg/l	0.114	0.137	0.158	0.114	0.182	< 0.2
		Pb mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	< 0.05
		As mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	< 0.05

Table (5):Variations of physicochemical parameters of alkaline ground water samples by influence of poly inorganic co-agulants based on silica

		Coagulant Parameters	G.W	PACSi	PAHSSi	PFeClSi	PAlFeClSi	Permissible Limit l
PHYSICAL PARAMETERS		colour mg/l	13	5	5	6	6	< 20
		TDS mg/l	507	716	779	797	726	< 1200
		Turbidity NTU	2.1	1.3	1.3	1.4	2.0	< 5
		EC μmohs/cm	788	1118	1206	1247	1133	< 1200
CHMICAL PARAMETERS		PH	7.37	8.26	0.08	8.19	8.26	6.5-9.2
	MAJOR ANIONS	CO_3^- mg/l	0.0	35.0	20.0	35.0	45	-
		HCO_3^- mg/l	305	347	395	350	347	-
		Cl^- mg/l	47	110	48	151	107	< 500
		SO_4^{--} mg/l	48	60	151	63	64	< 400
	MAJOR CATIONS	Na^+ mg/l	33.0	176	144	187	185	< 200
		K^+ mg/l	4.0	3.0	3.0	4.0	3.0	< 10
		Ca^{++} mg/l	86.0	38	78	52	26.0	< 200
		Mg^{++} mg/l	32.6	30.0	32.6	31.2	34.8	< 150
	NUTRIENT SALTS	NO_2^- μg/l	0.013	0.011	0.012	0.011	0.012	< 0.005
		NO_3^- μg/l	0.782	0.713	0.613	0.666	0.670	< 10
		NH_3 mg/l	0.03	0.02	0.03	0.02	0.02	-
		SiO_2 mg/l	28.40	20.70	16.20	24.60	20.10	-
		TP μg/l	0.410	0.095	0.077	0.069	0.109	-
	Heavy metals	Fe mg/l	2.5	0.1	0.05	0.09	0.008	< 1.0
		Mn mg/l	1.5	0.083	0.608	0.163	0.044	< 0.5
		Al mg/l	0.1	0.116	0.130	0.025	0.142	< 0.2
		F mg/l	1.0	0.87	0.93	0.13	0.01	< 0.8

Table (6) : Variations of physicochemical parameters of alkaline ground water samples polluted with arsenic lead , nitrate and fluoride by influence of poly inorganic co-agulants based on silica .

	coagulant / Parameters	G.W	PACSi	PAHSSi	PFeClSi	PAlFeCl Si	Permissible limits
PHYSICAL PARAMETERS	colour mg/l	13	8	7	5	6	< 20
	TDS mg/l	559	780	705	822	682	< 1200
	Turbidity NTU	8.7	1.9	1.8	1.2	1.4	< 5
	EC μmohs/cm	887	1204	1130	1278	1089	< 1200
CHMICAL PARAMETERS / PH	PH	7.45	8.33	7.58	7.67	8.07	6.5-9.2
MAJOR ANIONS	CO_3^- mg/l	0.0	45	0.0	25	10.0	-
	HCO_3^- mg/l	250	302	295	302	272	-
	Cl^- mg/l	65	118	67	145	115	< 500
	SO_4^- mg/l	84	124	168	120	92	< 400
MAJOR CATIONS	Na^+ mg/l	48	128	113	148	135	< 200
	K^+ mg/l	4.0	3.0	3.0	3.0	3	< 10
	Ca^{++} mg/l	86	80	80	80	54	< 200
	Mg^{++} mg/l	28.1	28.8	28.8	30.0	27.6	< 150
NUTRIENT SALTS	NO_2^- μg/l	0.389	0.039	0.026	0.020	0.039	< 0.005
	NO_3^- μg/l	7.731	1.947	2.313	2.911	1.634	< 10
	NH_3 mg/l	0.81	0.57	0.80	0.69	0.87	-
	SiO_2 mg/l	28.20	22.80	22.80	26.80	23.00	-
	TP μg/l	2.517	1.694	1.379	1.158	1.645	-
Heavy metals	Fe mg/l	2.1	0.063	0.044	0.049	0.097	< 1.0
	Mn mg/l	1.243	0.890	1.190	1.245	0.532	< 0.5
	Al mg/l	0.113	0.207	0.256	0.057	0.076	< 0.2
	Pb mg/l	13.559	1.613	1.860	0.319	1.533	< 0.0.5
	As mg/l	1.221	0.257	0.128	0.096	0.032	0.05
	F mg/l	2.889	3.429	2.966	3.017	2.892	0.8

Table (7):Effect of poly inorganic polymers based on silica of sewage waste water

		coagulant / Parameters	G W	PACSi	PAHSSi	PfeClSi	PalFeClSi	Permissible limits
Physical parameters		TDS mg/l	1500	1683	1700	1870	1599	< 2000
		TSS mg/l	550	40	47	40	39	< 50
CHMICAL PARAMETERS	pH			7.4	7.35	7.35	7.6	7.77	6.0-9.0
	OXYGEN STUDIES	COD mg/l	300	44.5	55.0	58.2	30.8	< 80
		BOD mg/l	200	25.1	40.0	35	16.5	< 50

Table (8) :Effect of poly inorganic polymers based on silica of
on industrial waste water

		Stations / Parameters	Spiked	PACSi	PAlFeCl	PAHSSi	PAlFeClSi	Permissible limits
	pH		3.5	8.97	8.68	7.05	8.65	6.0-9.0
		Pb mg/l	50.0	0.078	1.438	0.01	1.411	< 0.05
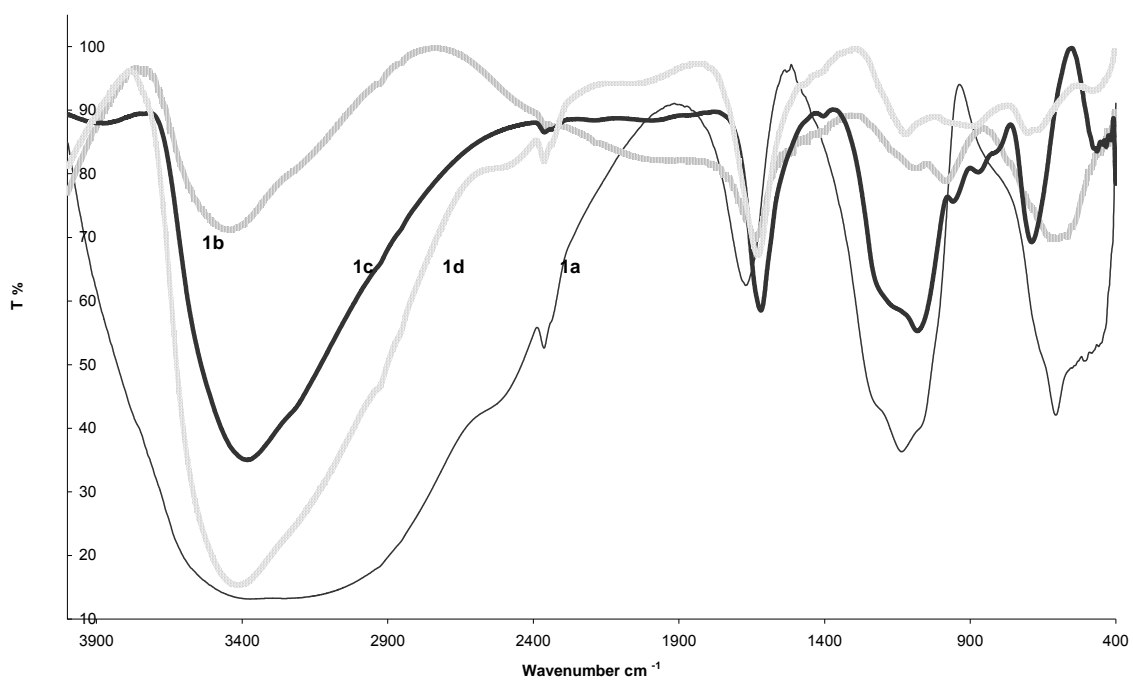
Fig. 1: FTIR spectra of a-.PAlHSSi, b- PAClSi, c -PFeClSi, d- PAlFeClSi
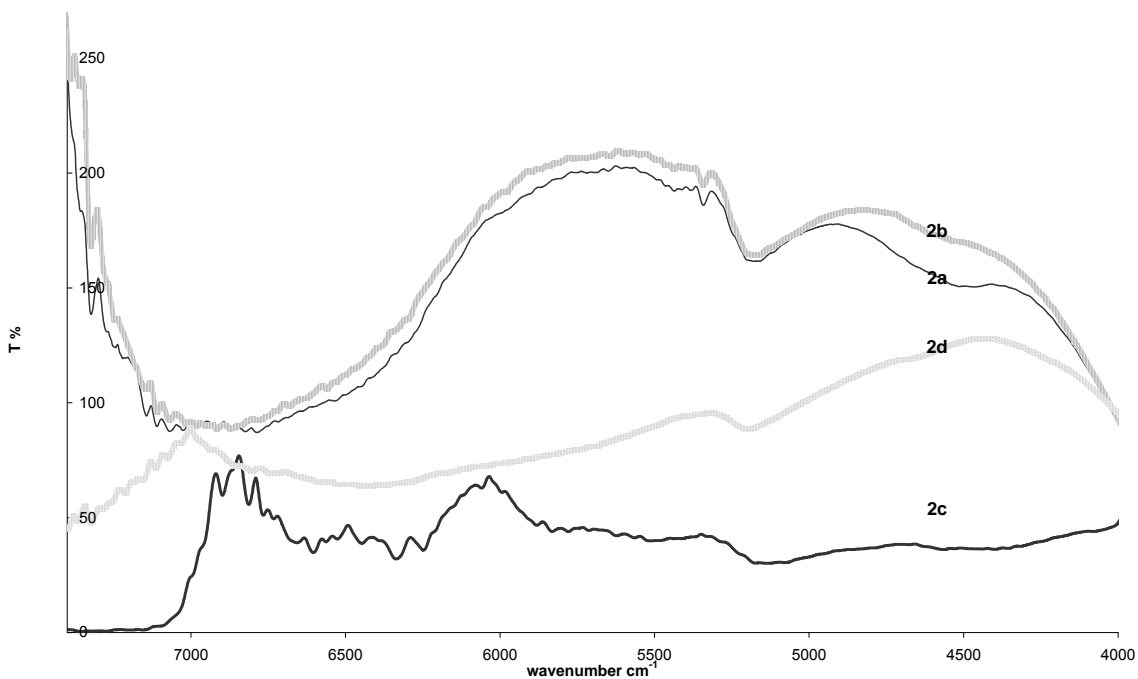
Fig. 2 : NFTIR spectra of a-.PACSi, b- -.PAHSSi, c -PFeClSi, d-PFeAlClSi

Fig. 3 : SEM micrograph of PACSi-C$_2$O$_4$ X100

Fig. 4: SEM micrograph of PACSi-SO$_4$X100

Fig. 5: SEM micrograph of PAHSSi X100

Fig.6 :SEM micrograph of PFeClSi X100

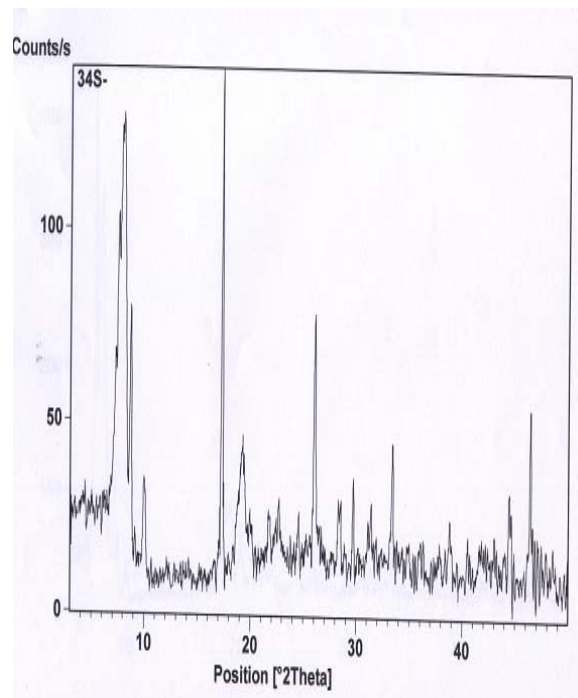Fig. 7: SEM micrograph of PFeAlClSi X100
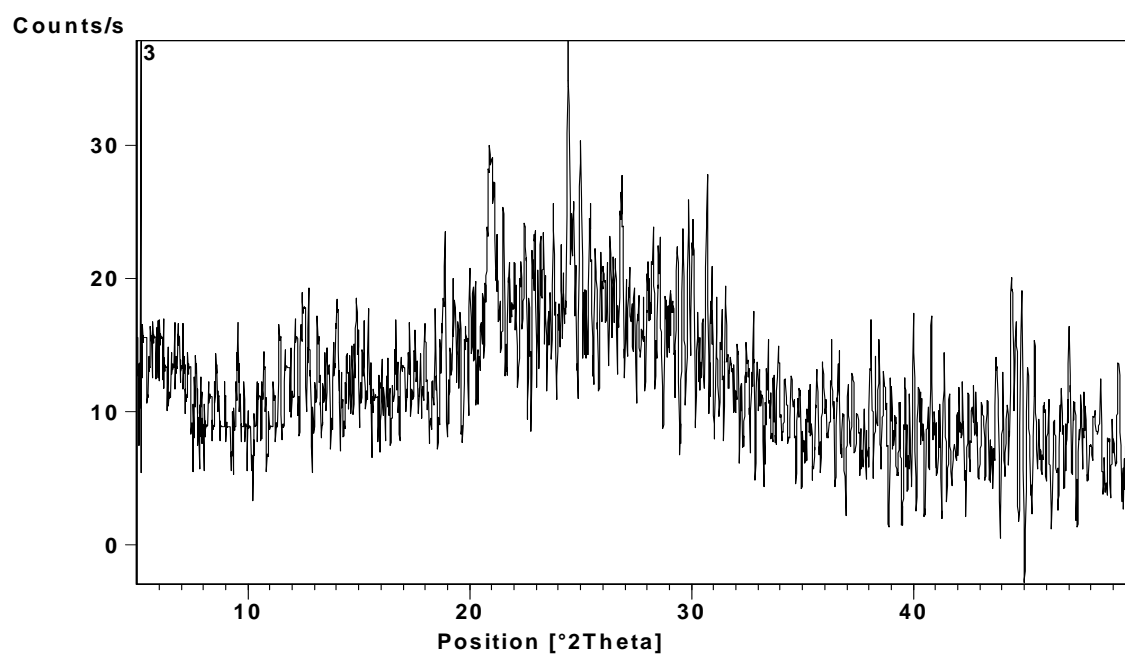

Fig. 8 : XRD diffractogram of PACSi
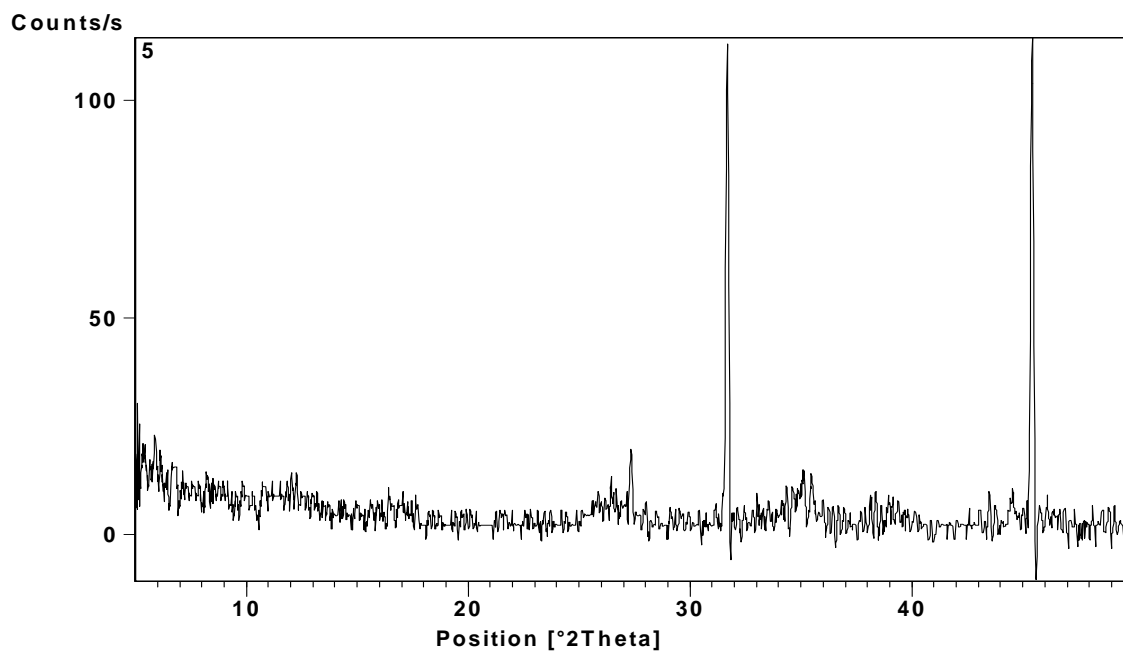

Fig. 9: XRD diffractogram of PAHSSi

Fig. 10 : XRD diffractogram of PFeClSi
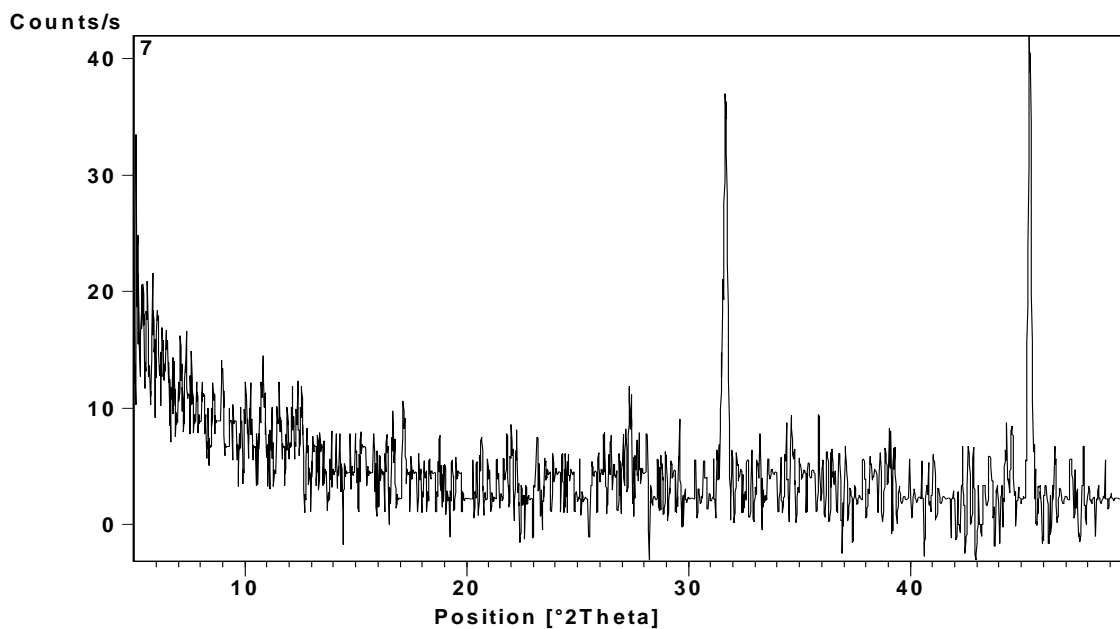
Fig 11 : XRD diffractogram of PFeAlClSi

REFERENCES:

[1]   J. Gregory, and J. Duan, Hydrolyzing metal salts as coagulants Pure Appl. Chem., **73**,. 2017–2026 (2001).

[2]   D. T. Richens. The Chemistry of Aqua Ions, ch.2, Wiley, Chichester (1997).

[3]   H.X. Tang, Basic studies of inorganic polymer flocculants, Environ. Chem. **9** 1–12 (1990).

[4]   D.S.Wang, H.X.Tang, J.Gregory, Relative importance of charge neutralization and precipitation during coagulation with IPF–PACl . Environ. Sci., Technol., 36 (8), 3866 (2002).

[5]   I.M. Solomentseva, N.G. Gerasimenko, S. Barany, Colloids Surf., **151,**113–126 (1999)

[6]   Y. Matsui, A. Yuasa, Y. Furuya, T. Kamei, J. Am. Water Wks Assn.**88** (10) 96–106(1996).

[7]   H.X. Tang, B.Z. Tian, Z.K. Luan, Y. Zhang, PFCl, in: R. Klute, H.H. Hahn (Eds.), Chemical Water and Wastewater Treatment (III),Springer-Verlag, 57–69 (1994).

[8]   H.X. Tang, Z.K. Luan, D.S. Wang, B.Y. Gao, Compsite inorganic polymer flocculant, in H.H. Hahn, et al. (Eds.), Chemical Water and Wastewater Treatment (V), Springer-Verlag ,24–33(1998).

[9]   D.S. Wang, H.X. Tang, Modified inorganic polymer flocculant-PFSi:its preparation, characterization and coagulation behavior, Water Res.,**35 (14)** 3418–3428(2001).

[10]   K. A Gray, C.H. Yao, C.R. O'Melia. J. Am. Water Wks Assn. **87 (4)** 136(1995).

[11]   H.X. Tang, Z.K. Luan, the different behavior and mechanism between inorganic polymer flocculant and traditional coagulants, in: H.H.Hahn, et al. (Eds.), Chemical Water and Wastewater Treatment (IV),Springer-Verlag, 83–93(1996).

[12]   J. Van Benschoten, J.K. Edzwald, Water Res. **24,** 1519(1990).

[13]   P.M. Bertsch, D.R. Parker, Aqueous polynuclear aluminum species, in: G. Sposito (Ed.), The Environmental Chemistry of Aluminum,CRC Press, 87–115(1996).

[14]   M.A. Blesa, E. Matijevic, Phase transformations of iron oxides, oxohydroxides, and hydrous oxides in aqueous media, Adv. Colloid Interface Sci. **29,** 173–221(1989).

[15]   R.M. Cornell, R. Giovdnoli, W. Schneider, Review of the hydrolysis of iron(III) and the crystallization of amorphous iron(III) hydroxide hydydrate, J. Chem. Tech. Biotechl. **46,** 115–134(1989).

[16]   P.M. Jardine, L.W. Zelazny, Mononuclear and polynuclear aluminum speciation through differential kinetic reactions with ferron, Soil Sci.Soc. Am. J. **50** 895(1986).

[17]   P.H. Hsu, D. Cao, Effects of acidity and hydroxylamine on the determination of aluminum with ferron, Soil Sci. **152 (3)** 210–219(1990).

[18]   D.R. Parker, P.M. Bertsch, Identification and quantification of the Al13 tridecameric polycation using ferron, Environ. Sci., Technol., **26,** 908(1992).

[19]   J. E Van Benchosten. and J. K Edzwald. Chemicala spects using aluminum salts. I. Hydrolytic reactions of alum and polyaluminum chloride. *Wat. Res***.** *24,*1519-1526(1990).

[20] A. K Arnold-Smith., R. M. Christie and C. Jolicoeur Polyaluminium silicate sulphate: a new coagulant for potable and waste water treatment. In Proceedings of the[5] International Gothenberg Symposium on Chemical Treatment, Springer-Verlag, New York, 203-222(1992).

[21] B.Y. Gaoa, H.H. Hahnb, E. Hoffmannb,* Evaluation of aluminum-silicate polymer composite as a coagulant for water treatment Water Research **36** 3573–3581(2002).

[22] T. Hasegawa, K. Hashimoto, T. Onitsuka, K. Goto, N. Tambo,Wat. Sci. Tech., **23** 1713(1991).

[23] K. Hashimoto, T. Hasegawa,O.T. Goto, N. Tambo, Water Supply **9,** 65(1991).

[24] B.Y. Gao, Q.Y. Yue, S.R. Wang, Chin. J. Environ., Sci., **11,** 37 (1990).

[25] Y. Matsui, A.Yuasa,Y. Furuya, T. Kamei, Dynamic analysis of coagulation with alum and PACl, J. Am. Water Works Ass., **90,** 96–106(1998).

[26] I.M. Solomentseva, N.G. Gerasimenko, S. Barany, Surface properties and aggregation of basic aluminium chloride hydrolysis products, Colloid Surf.A: Physicochem. Eng., Asp., **151,** 113–126(1999).

[27] S.K. Dentel, Coagulation control in water treatment, CRC Crit. Rev. Environ.Control, **21,** 41–135(1991).

[28] T. Tseng, B.D. Segal, M. Edwards, Increasing alkalinity to reduce turbidity,J. Am. Water Works Ass., ,**92,** 4–54(2000).

[29] M. Swiderska-Broz,M. Rak, On the importance of aluminum coagulant basicity in organic matter removal, in: H.H. Hahn, E. Hoffmann, H.Odegaard (Eds.), Chemical Water and Wastewater Treatment VII, IWA Publishing, London, 153–161(2002).

[30] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv., Colloidl nterface Sci., **100–102,** 475–502(2003).

[31] Z.K. Chowdhury, G.L. Amy, Coagulation of submicron colloids in water treatment by incorporation into aluminum hydroxide floc, Environ. Sci.,Technol., **25,** 1766–1773(1991)

[32] H.X. Tang, Z.K. Luan, et al., The differences of behavior and mechanism between pre-polymeric inorganic flocculants and traditional coagulants, in:H.H Hahn Ed. Chemical Water and Wastewater Treatment (IV), Springer Verlag, New York, 57–65 (1996).

[33] K.A. Gray, C.H.Yao, C.R. O'Melia, Inorganic metal polymers: preparation and characterization, J. Am. Water Works Ass., **87**, 136–146(1995).

[34] D.S. Wang, H.X. Tang, J. Gregory, Relative importance of charge neutralization and precipitation on coagulation of kaolin with PACl: Effect of sulfate ion, Environ., Sci., Technol., **36**, 1815–1820(2002).

[35] J.T. Kloprogge, R.L. Frost, Raman and infrared spectroscopic investigation of the neutralization of aluminium in the presence of monomeric orthosilicic acid Spectrochim. Acta **A 55** 1359-1369(1999).

[36] J. Theo Kloprogge *, Hu. Ruan, L. Ray Spectrochimica Acta., Part A **56**, 2405–2411(2000).

[37] J.T. Kloprogge, R.L. Frost, J. Mater Raman and infrared microscopy study of zunyite, a natural Al_{13} silicate. Sci., 5, 1505-1513(1999).

[38] Y., Xu , and etal Optimization of the separation and purification of Al13, Colloids and Surfaces Physicochem. Eng., Aspects, **231,1-9** (2003)

[39] B.j.,wang, S.G.wang   Wang, Shu-Guang Wang Characterization and coagulation of a polyaluminum chloride (PAC)coagulant with high Al_{13} content Journal of Environmental Management **76 ,**143–147 (2005).

[40] M. Muhammad and M. Wang ; NOVEL SYNTHESIS OF Al_{13}-CLUSTER BASED ALUMINA MATERIALS Nano structured material ,**11**, 1219-1229 (1999).

[41] R.A., Niehof, and G. I. Loeb. "The surface charge of particulate matter in sea water." Limnology Oceanography, **17**, 7(1992).