

Experimental investigation of coagulation process performance

Farshad Farahbod^{1*}, Aryan Abbasi²

¹Department of Chemical Engineering, Firoozabad Branch, Islamic Azad University, Firoozabad, Fars, (IRAN)

²Department of Chemistry, Damghan Branch, Islamic Azad University, Damghan, (IRAN)

E-mail : mf_fche@iauf.ac.ir, aryan_13b2@yahoo.com

ABSTRACT

In this paper a novel type of coagulant is studied. The coagulation process performance with using this type of coagulant is evaluated. This new type is the composition of zinc oxide nano particle and poly ferric sulfate (ZnOPFS). The structure of zinc oxide nano particles was characterized by FTIR, XRD and TEM, suggesting that ZnOPFS is a complex compound with mainly zinc oxide nano particles and ferric sulfate. The effects of Zn/Fe molar ratios (n) and aging time on the pH and zeta potential were also evaluated systematically. © 2015 Trade Science Inc. - INDIA

KEYWORDS

XRD;
FTIR;
TEM;
Nano.

INTRODUCTION

Concerns over resource shortages, increased environmental awareness and a preoccupation with environmental issues as a public relations matter have led many companies and individual producers to examine the efficiency and environmental compliance of their industrial processes. As one of the major vectors for pollution, the production of waste has been the focus of many of these studies and initiatives. In the case of liquid wastes, such as oily water, the double problem of wasting a resource as vital as water and discharging harmful pollutants into the environment has led to several waste water minimization techniques.

Source reduction

By far, the waste water reduction strategy with the greatest positive environmental impact is source reduction, reducing the amount of water used in an industrial process and, therefore, the amount of water discharged as waste.

Recycle and reuse

A second strategy for waste water reduction, recycling and reusing no hazardous liquid waste, allows an industrial process to reduce the amount of clean water used and the amount of waste water generated.

Treatment

End-of-pipe treatment is another important strategy in reducing industrial liquid wastes like oily water^[1,2]. Depending on the kind of oils dissolved in the water, a number of filtration and chemical processes can remove most or all of the oil suspended in the waste and create a stream of clean water that is less damaging to the environment and reusable for other processes^[3]. Even in household situations, simply running waste water through a sand filter even just a bucket of sand with some gravel and holes at the bottom can dramatically increase purity and turn waste water into a clean, usable resource^[4]. In this paper the coagulation process is evaluated.

Synergies and priorities

Poly acryl amide (IUPAC poly (2-propenamide) or poly (1-carbamoylethylene)) is a polymer ($-\text{CH}_2\text{CHCONH}_2-$) formed from acrylamide subunits. It can be synthesized as a simple linear-chain structure or cross-linked, typically using *N, N'*-methylenebis acryl amide. Poly acryl amide is not toxic. In the cross-linked form, the possibility of the monomer being present is reduced even further. It is highly water-absorbent, forming a soft gel when hydrated, used in such applications as polyacrylamide gel electrophoresis and in manufacturing soft contact lenses. In the straight-chain form, it is also used as a thickener and suspending agent. More recently, it has been used as a subdermal filler for aesthetic facial surgery. Polyacrylamide is a linear polymer comprised of monomers unit with functional groups of amide that adsorb on to the surface of particles. These particles are bridged together by the long polymer chain drawing the particles closer together. This process is called flocculation and is widely used in wastewater treatment. Poly acryl amide has the ability to bridge together particles suspended in solution by an adsorption process. Polymers often have electrostatic charges that allow for surface particle neutralization resulting in flocculation. When aqueous poly acryl amide solutions are mixed with sewage, the active amide groups on the polymer chain adsorb onto the surface of suspended material in the sewage and created bridges between them such that they now begin to exclude water from their newly formed structure. Once a small particle, now form larger flocs which can improve sedimentation rates in clarifiers, floatation rates in DAF systems and water removal in sludge thickening equipment. Poly acryl amide is widely used in domestic sewage treatment, mining tailings pulp & paper making, petrochemicals, chemicals, textiles, oil sands and mining industries. Also, a new type of inorganic flocculant, poly zinc silicate sulfate, was synthesized from silicate, sulfate, zinc and by co-polymerization. Comparative flocculation behaviors among poly-aluminium chloride, poly-ferric sulfate, poly silicate ferric and poly silicon boron ferric zinc sulfate were evaluated. The influences of temperature, acidity, storage time and dosage on flocculation were studied in different papers. The results show that com-

position of zinc oxide nano particle and poly ferric sulfate (ZnOFS) exhibits the best flocculation performance.

MATERIALS AND METHODS

All the applied chemical reagents were analytically pure and de-ionized water was applied to prepare all the solutions.

Synthesis method of nano-sized ZnO

Zinc metal is used to make a solution containing one molar Zn^{2+} ion. At first, this solution is purified, and then a type of surface-active reagent 0.05 M and approximately 10 per cent of ethanol is added under the ultrasonic conditions. The produced solution as agitated in certain time periodic. Same reagents are added to Na_2CO_3 , 1M solution under the same conditions. Then two produced aqueous solutions are mixed proportionally and agitating for half hour under the ultrasonic action. Sequentially, adding another surface-active reagent and agitating for half hour again, filtering and washing several times with distillation water and ethanol alternately under the ultrasonic action. The produced substance is prepared to dry for fifty minutes at 80°C . Then it roasted at 450°C for forty five minutes to obtain zinc oxide nano particles. The obtained produced substance has light yellow colour, and can be characterized by XRD, SEM and TEM. Produced spherical particles with the average diameter of 35 -55 nm in size are observed approximately and finally

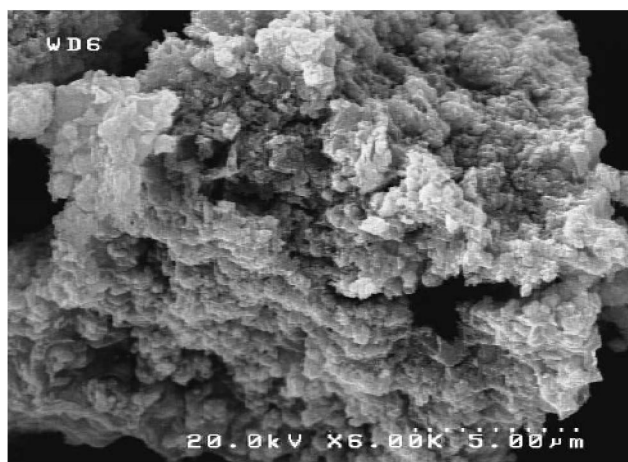


Figure 1-a : SEM photographs of zinc oxide nanoparticles on 5 μm scales

Full Paper

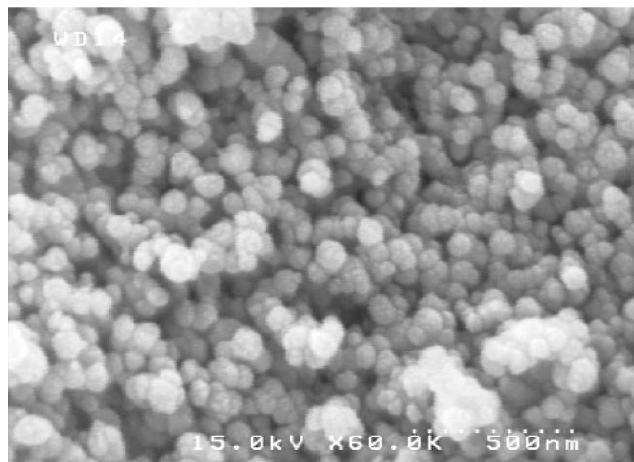


Figure 1-b : SEM Photographs of zinc oxide nanoparticles on 500 nm scales

the crystal is pure zinc oxide with hexahedral structure. Ultimately, the produced zinc oxide nanoparticles are added to poly ferric sulfate to prepare the novel substance as coagulant. Figure 1 shows SEM photos of zinc oxide nanoparticles in two different visions a) in the scale of 5 μm and b) in the scale of 500 nm.

Synthesis of poly ferric sulfate

As mentioned, the all of the reagents adopted in the synthesis of poly ferric sulfate were of analytic grade. The synthesis of poly ferric sulfate includes hydrolysis, oxidation, and polymerization, ultimately. The initial step was adding solid ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) into a 250 mL vial containing de-ionized water. Designated concentration of sulfuric acid was then introduced with the mole ratio of sulfuric acid to ferrous sulfate higher than 0.2:1 to prevent the precipitation of ferric oxide. After five min shaking, sodium chlorate (NaClO_3) was added as oxidant and the mixture was placed in a constant-temperature water bath accompanied with

TABLE 1 : Main properties of lab-prepared poly ferric sulfate

Parameters	pH	Density (g/cm ³)	Ferric content (wt. %)	Basicity (wt. %)
Value	2.9	1.3	13.5	10.7

continuous mixing at 200 rpm for 3 hours. The temperature was maintained between 55 °C and 80°C. Finally, the product was aged at 50°C for 2 hours to stabilize the PFS. The final product was in liquid form and reddish brown in color. The main charac-

teristics of the synthesized poly ferric sulfate were summarized in TABLE 1.

(a) Structure and morphology analysis

The solid poly ferric sulfate were grounded using a laboratory mortar and a pestle for characterization. So, the scanning electron microscopy was carried out applying a XL-30 EXEM. Fourier transform infrared spectra were obtained from spectrum 2000 FTIR spectrometer with the usual KBr pellet method.

(b) Fourier transform infrared spectroscopy (FTIR)

This is a proper and confident technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of fluid. The FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. The used FTIR has made dispersive infrared spectrometers all but obsolete (except sometimes in the near infrared), opening up new applications of infrared spectroscopy.

(c) X-ray scattering technique

XRD is a family of non-destructive analytical techniques which reveal information about the crystal structure, chemical composition, and physical properties of materials and thin films. This technique is based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy.

(d) Transmission electron microscopy (TEM)

The used method is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen and to be detected by a sensor such as a CCD camera. Obtained TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is thousands of times smaller than the

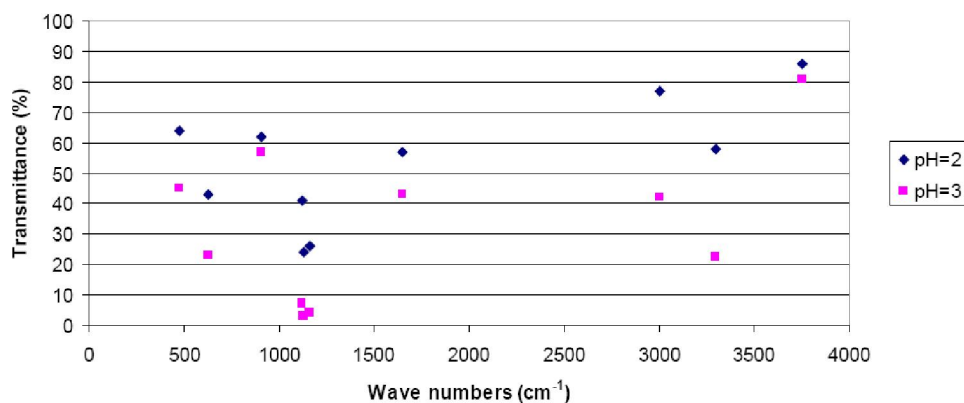


Figure 2 : FTIR spectra of ZnOPFS sample ($n = 2.0$) at different initial pH values (pH 2.0; pH 3.0)

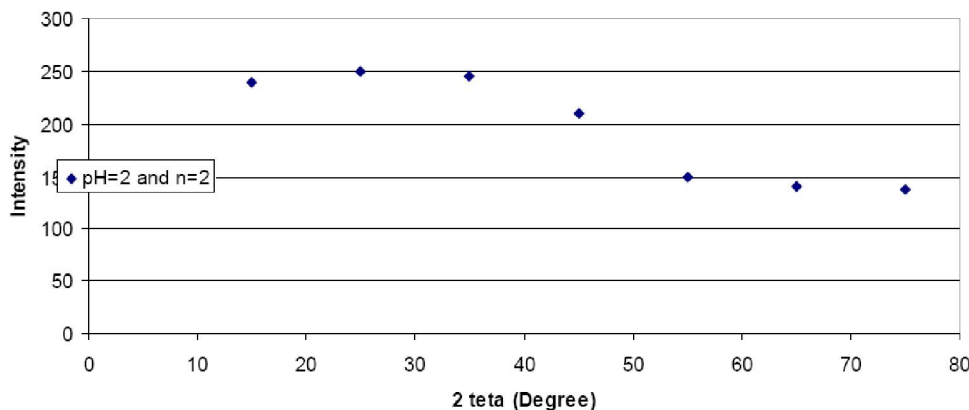


Figure 3 : XRD of ZnOPFS sample ($n = 2.0$, initial pH 2.0)

smallest resolvable object in a light microscope. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

RESULTS AND DISCUSSION

Structure and morphology

As mentioned, the SEM, XRD, FTIR and TEM were carried out to identify the structure of ZnO and PFS and to elucidate whether the influence factors affect its structure and morphology.

(a) FTIR spectra analysis

Figure 2 shows the FTIR spectra of ZnOPFSd (n

$= 2.0$) synthesized at pH 2.0 and 3.0, respectively. Both FTIR spectra analysis show two characteristics bonds at 3400–3350 cm^{-1} and 1642 cm^{-1} , which can be attributed to the stretching vibration of hydroxide anion and to the vibration of water absorbed, or complexes in the coagulant.

The peaks at 490 cm^{-1} and 1162 cm^{-1} are assigned to the characteristic bands for Zn–O bond and Fe–O bond, respectively. They also illustrate the characteristic peaks at 920 cm^{-1} and 620 cm^{-1} , which are attributed to the bending vibration of Fe–OH–Zn bonds. The stretching vibration of Fe–O bond is overlapped up by the absorption peak caused by the bending vibration of Fe–OH–Zn bond, indicating that zinc ion and its hydrolysis species have reacted with PFA to form zinc-ferric polymeric species. The peak at 1120 cm^{-1} is regarded as the crystal lattice vibration of SO_4^{2-} and HSO_4^- in ZnOPFS. As shown in Figure 2, at pH 3.0, the FTIR spectrum illustrates broad band for –OH, and shows the presence of functional groups. The peaks intensity at 1131 cm^{-1} and 1162 cm^{-1} (Fe–O) enhance with

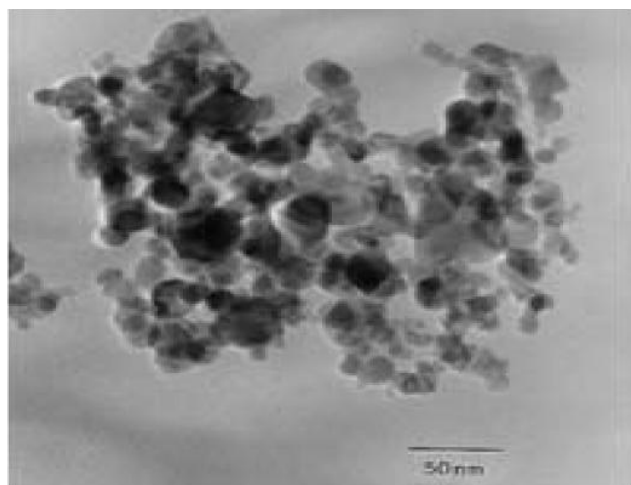


Figure 4 : TEM microphotographs of PZSS

lant could result in the discrepancy on intensity of absorption peak within the wave numbers of ZnOPFSd at different pH.

(b) XRD patterns and TEM analysis

Figure 3 shows the XRD of the ZnOPFSd powder. As shown in Figure 3, according to the PCPDFWIN analysis, very little reactants can be identified. This is due to that some peaks at 2 theta of 24.52 and 25.06 for ZnSO₄ as well as that of 23.14 and 30.45 for Na₂SiO₃·9H₂O are weak or barely observed. It is suggested that some new kind of compounds which are not included in the gallery or some new matter which does not give a standard formula

TABLE 2 : The different groups stability of ZnOPFS and PFA

Coagulant samples	pH	Zn/Fe ratio	Stability	Appearance
PFA1	1.5	0	14(D-T)	Gelation
PFA2	2	0	12(D-T)	Gelation
PFA3	2.5	0	9(D-T)	Gelation
ZnOPFSa1	1.5	0.5	42(D-T)	Precipitation
ZnOPFSa	2	0.5	-----	Transparent liquid
ZnOPFSa2	2.5	0.5	53(D-T)	Precipitation
ZnOPFSa3	3	0.5	35(D-T)	Precipitation
ZnOPFSb1	1.5	1	-----	Transparent liquid
ZnOPFSb	2	1	-----	Transparent liquid
ZnOPFSb2	2.5	1	50(D-T)	Precipitation
ZnOPFSb3	3	1	39(D-T)	Precipitation
ZnOPFSc1	1.5	1.5	-----	Transparent liquid
ZnOPFSc	2	1.5	-----	Transparent liquid
ZnOPFSc2	2.5	1.5	-----	Transparent liquid
ZnOPFSc3	3	1.5	38(D-T)	Precipitation
ZnOPFSd1	1.5	2	-----	Transparent liquid
ZnOPFSd	2	2	-----	Transparent liquid
ZnOPFSd2	2.5	2	55(D-T)	Precipitation
ZnOPFSd3	3	2	32(D-T)	Precipitation

(—) means; No precipitation occurs within 60 days; (D-T) means; De-stabilized time (day).

increasing the pH, implying that the Fe–O–H bond strength is improved and the amount of poly-nuclear and hydrolyzed polymer are increased. The ratio of absorption peak intensity at 920–1162 cm⁻¹ increase with the increasing of pH, indicating increase in the number of Fe–OH–Zn bonds and poly-nuclear polymer in ZnOPFS sample; in other words, increase in the pH causes to the enhancement of aggregation degree, and thus, the diversities on structure of coagu-

may be have been formed. Most peaks of strong intensity occur at 2 theta of 16.20, 19.22, 20.80, 25.98, 26.99 and 34.03, this is an indication that ZnOPFS should be a new poly crystalline compound of Fe, Zn and other polymeric species, rather than a simple mixture of raw materials.

As shown in Figure 4, the morphologies of ZnOPFS solution possess the compact net structures with some hydrolytes which are different from that

of PFA, and the compact extent of net structure enhances with increasing n within a range. The compact net structure is more favorable to coagulate colloidal particles and form bridge-aggregation among flocs when compared with the branched structure. The above results suggest that the structure of ZnOPFS is affected by n value, which can form various hydrolysates and polymeric species accordingly. However, if n exceeds 2.5, liquid ZnOPFS samples precipitate during a short aging period. Overall, the FTIR, XRD and TEM analysis of ZnOPFS samples show that the pH and n value have strong influences on the structure and morphology of the samples and, consequently, the preparation of ZnOPFS and its coagulation performance should be based on these parameters.

Properties of ZnOPFS

(a) Stability of the ZnOPFS

In view of the instability of PFA solution, metal ions are generally considered as polymerization retardants. They can control the reaction rate of PFA and prevent gelation, and accordingly improve the stability of poly ferric. This is attributed to that the addition of metal ions may decrease the amounts of H_4FeO_4 , and thus reduce the polymerization rate of PFA. On the other hand, the electron cloud density of hydroxyl group in the PFA molecule is dispersed, which can reduce the polymerization rate of PFA. The stability of the samples was observed under room temperature and the results are summarized in TABLE 2. It can be noticed that the stability of ZnOPFS is markedly improved compared to that of PFA. On one hand, PFA has a steady period within 9–14 days at pH 1.5–2.5, and then the samples finally become gelation.

On the other hand, some of the ZnOPFS samples have been stored steadily more than 60 days without precipitation and gelation. However, there are some precipitations in the ZnOPFS samples at pH 3.0 within 40 days. This can be attributed to the fact that PFA species in ZnOPFS generate gelation as the pH increases.

CONCLUSIONS

A novel coagulant was synthesized by zinc oxide nano particle and poly ferric sulfate (ZnOPFS). The analysis of FTIR, XRD and TEM indicate that the reactions among zinc and ferric are not simple physical blends, but the complexation forming inorganic polymeric species. Furthermore, the structures of ZnOPFS are dependent on the n value and pH. The stability test shows zinc ion can prevent the gelation of poly ferric acid and improve the stability of ZnOPFS.

REFERENCES

- [1] A.D. Butler, M. Fan, R.C. Brown, J. VanLeeuwen, S. Sung, B. Duff; Pilot-scale tests of poly ferric sulfate synthesized using SO_2 at Des Moines Water Works, Chemical Engineering and Processing, **44**, 413–419 (2013).
- [2] O.S. Amuda, I.A. Amoo; Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment, Journal of Hazardous Materials, **141**, 778–783 (2013).
- [3] J. Duan, John A. Gregory; Coagulation by hydrolysing metal salts, Advances in Colloid and Interface Science, **100**, 475–502 (2012).
- [4] Jia-Qian Jiang, Barry Lloyd; Progress in the development and use of ferrate (VI) salt as an oxidant and coagulant for water and wastewater treatment, Water Research, **36**, 1397–1408 (2012).