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Investigating the Performance of the Coagulation Process When Using a Combination of Zinc Oxide Nanoparticles and Ferric Polysulfate

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Abstract

In this article, a new type of coagulant material has been investigated and the performance of the coagulation process using this type of coagulant was evaluated. This new type is a combination of zinc oxide nanoparticles and polyferric sulfate (ZnOPFS). The structure of zinc oxide nanoparticles was determined by spectroscopic, X-ray and electron microscopy methods, and based on this, it was determined that ZnOPFS is a complex and mixed compound that is mainly composed of zinc oxide nanoparticles and ferric sulfate. The effects of Zn/Fe (Zn/Fe) molar ratio and aging (time) on acidity and zeta potential were also evaluated using a specific method. The obtained results showed that in the simultaneous deposition process, zinc ions can prevent the formation of polyferric acid coagulation and subsequently improve the stability of ZnOPFS.

Keywords

Nano Polymer, Coagulant, Ply Ferric, ZnOPFS, pH

1. Introduction

Concerns about issues such as the lack of resources, increasing environmental awareness, and the concern of environmental issues becoming a public issue, have caused many companies and individual producers to examine the efficiency and compatibility of the environment [1]-[21]. Environment of their industrial processes. Waste production as one of the important carriers of pollution has

been the focus of many studies and projects. Regarding liquid waste such as water contaminated with oily substances, the double problem is the loss of a vital resource such as water and the discharge of harmful pollutants to the environment, which leads to the use of various methods of water minimization [22]-[43]. In fact, one of the strategies to reduce polluted water with the greatest direct environmental impact is to reduce resources, which means reducing the amount of water used in industrial processes and therefore reducing the amount of water discharged as waste [44]-[56]. This process mainly includes the identification of processes such as washing, cooling and dissolution of chemical compounds in which water is the main element and also determining the minimum amount of water required to complete the mentioned processes [57]-[69]. Reducing the flow of wastes, in potentially harmful liquid wastes such as water contaminated with oily substances that require special disposal and purification, also reduces the disposal space or the required purification energy to neutralize the wastes [70]-[86]. Cleaning the surfaces with a dry cloth, even in everyday tasks such as oiling metal parts, reduces the amount of water and residues contaminated with oily substances and increases the lifespan of many oil lubricants.In order to reduce polluted water, recycling and reuse of liquid waste is harmful, which allows industrial processes to minimize the amount of clean and healthy water used and then reduce the amount of polluted water produced. It is not necessary that the water needed to cool the car parts be completely clean in order to have a better and more effective operation. Therefore, the use of relatively polluted water for various purposes leads to a general reduction of water consumption and waste production, and even in smaller-scale processes, to clean multiple surfaces, using a bucket of water instead of leaving water (running water), water consumption And it significantly reduces the volume of water contaminated with oily substances [87]-[91]. In general, digging the ground to reach the desired goal is called digging. Drilling can be done to reach oil, water, gas, etc. In the oil industry, drilling operations are carried out at a very high speed, because the use of a drilling rig for a long time is economically very expensive. Drilling operation is very dangerous and the most experienced people are always used to do this work [92]-[96]. Determining the drilling location in the oil industry is done by geological engineers, and after that, the drilling operation begins in coordination with the reservoir engineers and determines the exact location of the oil. After the successful completion of exploration operations, drilling operations are carried out during all stages of oil field development and in all environments [97] and [98]. Drilling is one of the most complex, expensive, exhausting and specialized jobs in the oil industry. Basically, any work done before drilling is useless if the drilling is not done properly. Therefore, digging is given great importance. Depending on different conditions and situations, different methods are used for drilling wells, each of which has certain advantages and disadvantages. On the other hand, along with the progress and development of science and technology, extensive research is being done in the field of drilling by various companies, institutions and governments. There is a possibility of

using some research projects in the next few years. Not only the existing drilling methods are constantly changing and evolving, but new drilling methods are also emerging. Drilling with the help of nuclear energy or ultrasonic drilling are among the cases that can actually be called as new methods that are in the research stage and are used for specific applications [99] [100] [101] [102].

In this article, a new type of coagulant material has been investigated and the performance of the coagulation process using this type of coagulant was evaluated. This new type is a combination of zinc oxide nanoparticles and poly ferric sulfate (ZnOPFS).

2. Materials and Methods

2.1. Nano Polymer Synthesis

All the reagents used in ferric polysulfate synthesis were analytically graded. The synthesis of ferric polysulfate includes the processes of dehydration, oxidation and finally, sintering. The first step is to add solid ferrous sulfate ($FeSO_4 \cdot 7H_2O$) to 250 mL of deionized water. Then, a 0.5 M of sulfuric acid with a molar ratio higher than 0.2:1 compared to ferrous sulfate was added in order to prevent precipitation of ferric oxide. After shaking for 5 minutes, sodium chlorate ($NaClO_3$) was added as an oxidant, and the obtained mixture was kept in a water bath (Bain-Marie) with a constant temperature, which was continuously stirred at a speed of 200 rpm for a period of 3 hours were placed. The temperature was kept between 55˚C - 808˚C. Finally, in order to stabilize PFS, the product was exposed to 508˚C for 2 hours. The final product was liquid and reddish-brown in color. The characteristics of solid ferric polysulfate were determined based on the use of a mortar in a laboratory environment. Hence, scanning electron microscope (SEM, Model: FEI Altura 810) test was performed using XL-30 EXEM. In order to calculate the Fourier transform infrared spectrum, 2000 Fourier transform infrared (FTIR, Model: LAB 5500) spectrometer was used in the usual KBr method (potassium bromide tablets).

2.2. Fourier Transform Infrared Spectroscopy

This is a special and reliable method for calculating the infrared spectrum related to the absorption, emission, illumination and Raman scattering of fluids. The FTIR spectrometer has the ability to simultaneously collect spectral data related to a wide spectral range; the advantage of this spectrometer compared to the sputtering spectrometer is the same. A sputtering spectrometer is a device that measures the intensity of a limited range of wavelengths in a period of time. The used FTIR method has made almost all infrared sputtering spectrometers unusable except when they are near infrared and provides new fields for the use of infrared spectroscopy. For the preparation of Fe-chelated aspartate (Fe-Asp), the method ascribed by [48] was followed. Briefly, 260 g $FeSO_4 \cdot 7H_2O$ was added and dissolved in dH_2O. Then, L-aspartate monohydrochloride (146.12 g) was added and warmed well at 95˚C for 3 h. The chelation was confirmed by FTIR analysis as shown in **Figure 1**.

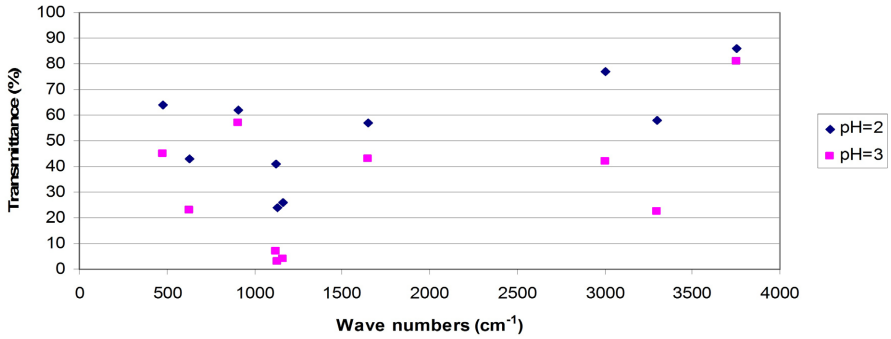


Figure 1. FTIR spectrum of ZnOPFS sample (N = 20) at different initial pH values (pH = 3) (pH = 2).

2.3. X-Ray Diffraction Method

The X-Ray Diffraction (XRD) is one of the non-destructive analytical methods that can be used to obtain information about the crystal structure, chemical composition and physical properties of materials and thin layers. This method is based on examining the scattering intensity of X-ray rays when they hit a sample and provides information such as the angle of impact and scattered rays, polarization, wavelength and energy.

3. Results and Discussion

3.1. FTIR Spectrum Analysis

Figure 1 shows the FTIR spectrum related to the synthesis of ZnOPFSd (n = 2.0) at pH = 2 and pH = 3, respectively.

The analysis and investigation of both FTIR spectra shows the bonding characteristics in the range of 3400 - 3350 cm^{-1} and 1642 cm^{-1}, which can be caused by the stretching.

Vibration of hydroxide anion, water absorption vibration or coagulant material complexes. The peaks in the regions of 490 cm^{-1} and 1162 cm^{-1} are related to the characteristics of Zn-O bond and Fe-O bond, respectively. In addition, specific bending vibration peaks for Fe-OH-Zn bonds are located in the region of 920 cm^{-1} and 620 cm^{-1}. The stretching vibration of the Fe-O bond overlaps with the absorption peak caused by the bending vibration of the Fe-OH-Zn bond. This overlap indicates the reaction of zinc ions and its hydrolyzed species with PFA in order to form zinc-ferric polymer species. The peak in the region of 1120 cm^{-1} is related to the lattice vibration of SO_4^{2-} and HSO_4^- crystals in ZnOPFS. As shown in Figure 1, the FTIR spectrum at pH = 3 shows the wide bond of -OH and functional groups. Stronger peaks for (Fe-O) at 1131 cm^{-1} and 1162 cm^{-1} and with increasing pH are observed and indicate the strengthening of the Fe-O-H bond strength and the increase in the number of polycyclic and hydrolytic polymers. With the increase in pH, the intensity of the absorption peak at 920 - 1162 cm^{-1} increases. This indicates an increase in the number of Fe-OH-Zn bonds and polycyclic polymers in the ZnOPFS sample. In other words, the pH value increases the amount of aggregation and cohesion of par-

ticles, and as a result, the difference in the structure of the coagulants can lead to the difference in the intensity of the absorption peak in the wave numbers of ZnOPFS at different pH.

3.2. XRD Patterns and TEM Analysis

Figure 2 shows the XRD spectrum of ZnOPFS powder. As Figure 2 shows, very few reactants can be detected with the help of PCPDFWIN software. The reason for such a situation can be the presence of weak or low peaks of $ZnSO_4$ in and $Na_2SiO_3{\cdot}9H_2O$ in and it has been suggested that the reason for the existence of these peaks may be the formation of new compounds that are not part of the existing groups or new substances that do not yet have a standard formula. Most of the peaks with high intensity occur in the region and it indicates that ZnOPFS must be a new polycrystalline compound of Fe, Zn and other polymer species and not a simple mixture of raw materials.

As shown in Figure 3, based on the morphology of ZnOPFS, it was determined that this composition has a dense network structure with some hydrolytic materials that are different from the materials in PFA, and with increasing n in a range increases the compression of the network structure. Examining the atomic structure of this compound confirms this issue. In order to flocculate colloidal particles and form aggregate bridges between clots, dense network structures are much more favorable than branched structures. According to the aforementioned results, it can be said that the structure of ZnOPFS is strongly influenced by the value of n, which causes the formation of different hydro caves and the formation of polymer species in the same proportion. However, if it is, the ZnOPFS liquid samples will need a short aging period to settle. In general, the results of examining ZnOPFS samples with the help of FTIR, XRD and TEM methods showed that pH and n value have a great effect on the structure and morphology of the samples and hence, in order to prepare ZnOPFS and Examining its coagulation function should pay attention to these factors.

3.3. Properties of ZnOPFS

Due to the instability of PFA solution, metal ions are generally considered as

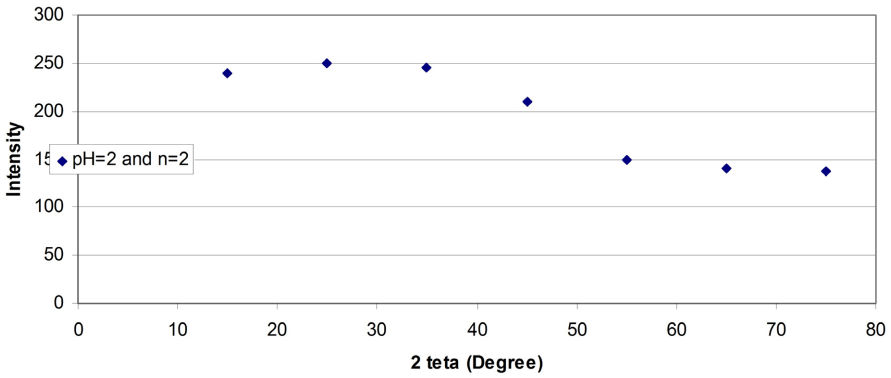


Figure 2. XRD spectrum of ZnOPFS sample (n = 2.0 and initial pH = 2.0).

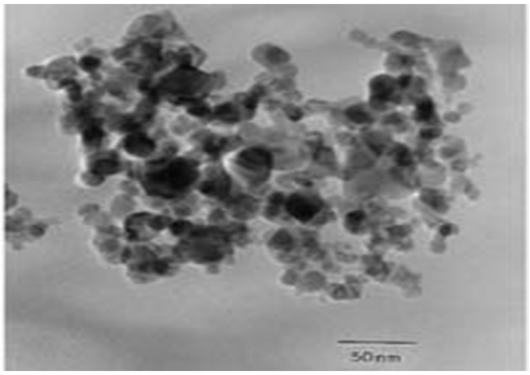


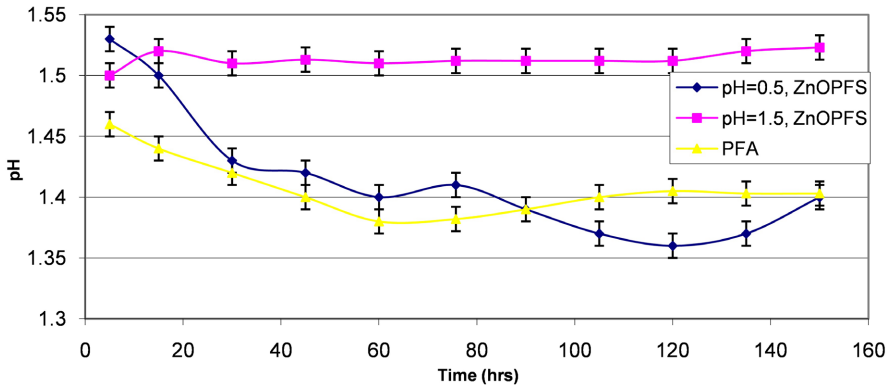
Figure 3. TEM photo in micro dimensions of PZSS.

factors that slow down the sintering process. On the other hand, these ions can control the speed of PFA reaction and prevent coagulation and thus improving the stability of polyferric. The occurrence of such situations is because the increase of metal ions causes a decrease in the amount of H_4FeO_4 and, as a result, a decrease in the amount of PFA deposition. On the other hand, the super-electron density of the hydroxyl group of the PFA molecule is lost and can reduce the amount of PFA deposition. It was observed that the stability of ZnOPFS has increased significantly compared to the stability of PFA. On the other hand, the stability of PFA at pH = 1.5 - 2.5 is 9 - 14 days, and then the samples finally turn into gel.

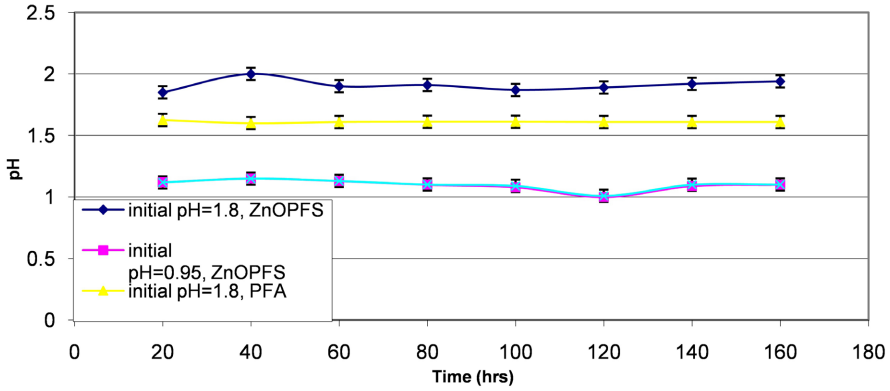
3.4. Change in Acid Strength during the Aging Period of ZnOPFS

Although the stability of ZnOPFS is increased compared to PFA, their coagulation functions may gradually decrease during the final storage period due to the change of coagulant structure. During the aging time, the changes in pH reflect the changes in the polymer species and the morphology of the coagulants. **Figure 4(a)** shows the pH changes of two ZnOPFS and PFA samples at the same initial pH. It can be seen that they are strongly dependent on time, that is: the acid strength (pH) of PFA decreases all the time and gradually becomes saturated after 60 hours; However, the acid strength (pH) of ZnOPFS increases first, but after passing the maximum value, it decreases and finally becomes stable. In addition, changing the value of n in ZnOPFS leads to the divergence of time-dependent pH behaviors: at n = 0.5, the affinity and pH saturation of ZnOPFS is similar to PFA after 20 hours. However, at n = 1.5 the pH is close to the initial value throughout. Before reaching the steady state, the pH changes due to the fact that the dehydration/sintering reactions are still taking place.

Then, the pH (acidic strength) of ZnOPFS is gradually fixed, and this means that the dehydration/deposition stage is over and ZnOPFS has reached a relative equilibrium state. According to the data in **Figure 4(a)**, it can be said that the species present in ZnOPFS can greatly affect the amount of pH changes: the deposition of zinc ions leads to an increase in pH in the early aging period. To be in the same way, the decrease in pH can be caused by the curing process. **Figure 4(b)**



(a)



(b)

Figure 4. Effect of aging time on the pH changes (a) and (b).

shows the effect of aging time on the pH changes of coagulants at different initial pH. The similarity of the pH changes related to ZnOPFS and PFA at the initial pH of 0.95 can be the reason for the possible similar behavior in aqueous solutions and polymer species in ZnOPFS and PFA. However, differences are also evident in the initial pH of 1.80 for ZnOPFS and PFA, which include: the pH of PFA gradually decreased and finally stabilized at a value lower than 1.80. Unlike PFA, the pH of ZnOPFS increased gradually and reached stability at pH = 1.98. It is worth mentioning that the difference in pH of coagulant materials is due to the great effect of pH on the formation and transformation of some species in ZnOPFS. Although at pH = 0.95, the characteristic distribution of ZnOPFS samples is similar to that of ferric, but at pH = 1.80, the primary ferric species in ZnOPFS change rapidly after the aging process. With the increase of pH, monomer species, low polymer (Fe-a), medium polymer (Fe-b) and high polymer (Fe-c) in ZnOPFS samples are not longer than their similar species in single PFA solutions. Rather, all of them are being complexed or combined with the species in Frick. With the increase in pH, the amount of Fe-b and Fe-c increases, and this indicates that with increasing alkalinity, the composition between ferric and zinc-ferric hydrostatic species increases. Therefore, such cases lead to a difference in pH between coagulants.

4. Conclusion

A new coagulant was synthesized using zinc oxide nanoparticles and ferric polysulfate (ZnOPFS). The analysis of the results of FTIR, XRD and TEM tests showed that the reactions between zinc and iron (ferric) are not only of the type of simple physical dilution, but also of the type of complex formation of inorganic polymer species. In addition, the structure of ZnOPFS depends on the value of n and pH. The stability test results showed that zinc ions can prevent the coagulation of polyferric acid and increase the stability of ZnOPFS. By examining the pH changes of the ZnOPFS liquid during the aging stage, it can be concluded that when the processes of dewatering/commissioning reach a relatively stable state, the pH usually remains constant. Investigation of zeta potential showed that pH and n value have a great effect on ZnOPFS charge. The increase of zinc ions increases the positive charge of ZnOPFS, which is needed to neutralize the charge of colloidal particles in diatomite suspension and wastewater contaminated with oily substances.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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