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Preparation of High Effective Flocculant for High Density Waste Drilling Mud

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ABSTRACT

To satisfy the requirement on the separation of solid and liquid in waste drilling mud, prepare a high effective flocculant for high density waste drilling mud used starch, 2-*Trimethylammonium ethyl methacrylate chloride* (*DMC*) *and acrylamide* (*AM*). *The result showed that when the ratio of starch, DMC and AM was* 2:1:3, *the weight of initiator* (*potassium persulfate*) *was* 0.2% *of the AM, reaction temperature was* 65℃ *and reaction time was* 5*h, the performance of product was the best. The water content in filter cake was* 27.6% *after the waste drilling mud disposed by the optimization flocculant. The flocculent effect of optimization flocculant was superior to that of other flocculant in market.*

Keywords: *High Density, Waste Drilling Mud, Dispose, Cation*

1. Introduction

The waste drilling mud and drilling wastewater were the inevitable industrial waste while Oil and Gas Exploration Drilling. They has become one of the most severe pollution sources, whose effect on environment has been concerned gradually [1-3].There were many methods [4-7] to dispose the waste drilling mud and drilling wastewater, such as, Gravity Separation, Impact, Baffle, or Spray Separation, Parallel-Plate and Thin-Film Separation and Vacuum Separation. The Solid-Liquid Separation has such advantages as large capacity, simple operation and using a few equipments [8], it was the most important and Widely Application method. At deep well drilling, the component of waste drilling mud was more and more complexity, the density of waste drilling mud was higher, and the waste drilling mud treatment was more harder [9]. The flocculant in market has not deal with the high density waste drilling mud. So a new starch-based cation copolymer flocculant for high density waste drilling mud was prepared.

2. Methods

2.1 Agent

Edible corn starch, 2-Trimethylammonium ethyl methacrylate chloride (CP), acrylamide (A.R), potassium persulfate (A.R), sodium hydroxide (A.R).

High density waste drilling mud, the density was 1.639 g/mL and the Solid content was 56.72%.

2.2 Synthesis of Starch-Based Cation Coploymer Flocculant

Add some deionized water, corn starch and sodium hydroxide into a three-neck flask with stirrer. Heat the system to 70˚C and stir until starch dissolved completely (about 30 min), then cool the system to room temperature and removal of oxygen dissolved in the solution by blowing continuously nitrogen. After add some AM and DMC into above system, add the potassium persulfate solution drop by drop. Keep the system react for a certain time at a given temperature to gain product.

2.3 Flocculent Treatment

Add some gel breaker to some waste drilling mud, then add some flocculant to above system and stir, centrifugal separation (3500 r/min) for 10min. Weight the quality of filter cake (m1) and soild phase (m2) after baking, gain the water content in filter cake by the formula as follows: the water content in filter cake = (m1-m2)/m1.

3. Result and Discussion

3.1 Preparing Conditions of Starch-Based Cation Copolymer Flocculant

3.1.1 Appropriate Weight Ratio of AM and Starch

The amount of starch was 3 g, DMC dosage was 1 mL, pH = 7, the reaction temperature was 70˚C, reaction time was 3 h, the amount of acrylamide was respectively 3 g, 6 g, 9 g, 12 g, the amount of potassium persulfate was

0.2% of the quality of acrylamide. The flocculent effect is shown in **Figure 1**.

Figure 1 showed when m(AM)/m(starch) = 3, the water content in filter cake was the minimum (32.3%). When the m(AM)/m(starch) above 3, the lesser quality of starch made the active sites for graft reaction decrease, so the molecular weight of copolymer diminished. The Low Molecular Weight copolymer could not link tightly with solid matter in waste drilling mud, so the flocculation effect was not good.

3.1.2 Appropriate Dosage of DMC

The starch quality was 3 g, the quality of acrylamide was 9 g, pH = 7, the reaction temperature was 70˚C, reaction time was 3 h, the amount of potassium persulfate was 0.2% of the quality of acrylamide, DMC dosage respectively was 1 mL, 2 mL, 3 mL, 4 mL. Study the effect of DMC dosage on the water content in filter cake (**Figure 2**).

Figure 2 showed when the DMC dosage was 2 ml, the water content in filter cake was the lowest. Increasing the dosage of DMC make the cationic degree of copolymer increase. The clay in waste drilling mud charged negative, so the higher of the cationic degree of copolymer was, the more the negative charge neutralized, so the solid matter in waste drilling mud was more easier to separate from waste drilling mud. But when the DMC dosage was greater than 2 mL, the water content in filter cake increased. The reason maybe as follows:

1) Impact of Cl^-: The initiator was $K_2S_2O_8$, Cl^- can react with $S_2O_8^{2-}$ to form Cl_2, Cl atom can act as a chain termination agent, so that the molecular weight of copolymer decreased.

2) Steric Hindrance Effect: DMC with Steric Hindrance reduce the probability of collision between DMC monomer and chain free radical.

Above two factor increase the difficult of Polymerization between DMC and starch and AM, so the flocculation effect was not good.

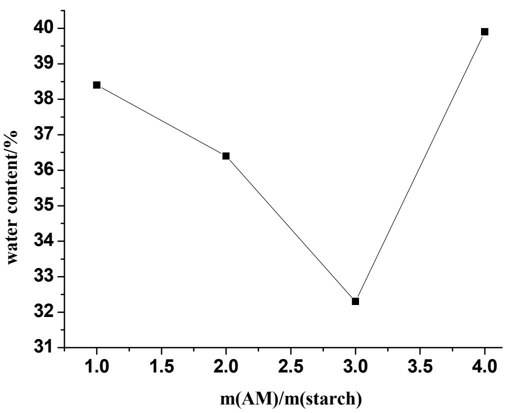


Figure 1. The effect of m(AM)/m(starch) on water content in filter cake

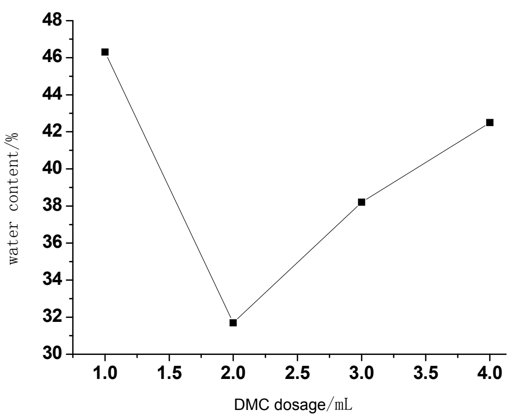


Figure 2. The effect of DMC dosage on water content in filter cake

3.1.3 Appropriate Dosage of Initiator

The amount of starch was 3 g, DMC amount was 2mL, the amount of acrylamide was 9 g, pH = 7, the reaction temperature was 70˚C, reaction time was 3 h. The amount of potassium persulfate was respectively 0.1%, 0.2%, 0.3%, 0.4%, 0.5% of the quality of acrylamide. The flocculent effect is shown in **Figure 3**.

From **Figure 3** we can see that when the potassium persulfate dosage was 0.3%, the water content in filter cake was the lowest. Because when the amount of potassium persulfate increased, the concentration of free radicals increase, grafting reaction rate accelerated, graft product molecular weight was larger. But when the quality of potassium persulfate was more than 0.3% that of acrylamide monomer, the water content of filter cake actually increased. The increasing concentration of potassium persulfate caused homopolymerization reaction probability of monomer increase and the termination of free radicals also increase, so the copolymer molecular weight was not big enough and the water content in filter also increased.

3.1.4 Reaction Time

The amount of starch was 3 g, DMC amount was 2 mL,

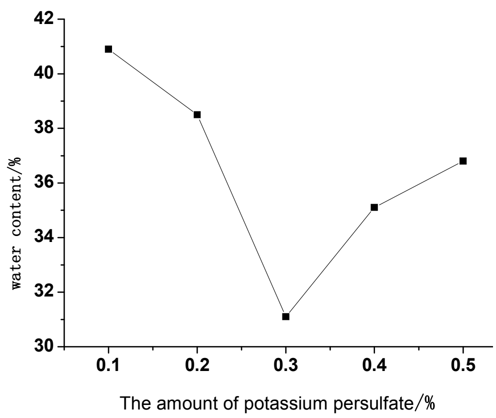


Figure 3. The effect of potassium persulfate dosage on water content in filter cake

the amount of acrylamide was 9 g, pH = 7, the amount of potassium persulfate was 0.3% of the quality of acrylamide, reaction temperature was 70˚C, the reaction time was respectively 3 h, 4 h, 5 h, 6 h, 7 h. The flocculent effect is shown in **Figure 4**.

As can be seen from **Figure 4**, the best reaction time was 4 h, this was because early in the reaction system, the active center of grafting reaction was more, the reaction rate was quick. But when the reaction time was more than 4 h, the number of grafting points decreased, which made grafting reaction rate slow down, so the grafting yield had fallen and the water content in filter cake correspondingly increased.

3.1.5 Reaction Temperature

The amount of starch was 3 g, DMC amount was 2 mL, the amount of acrylamide was 9 g, pH = 7, the amount of potassium persulfate was 0.3% of the quality of acrylamide, reaction time was 4 h, the reaction temperature was respectively 50˚C, 55˚C, 60˚C, 65˚C, 70˚C, 75˚C. The flocculent effect is shown in **Figure 5**.

The reaction temperature at 65˚C, the water content in filter cake was the lowest. Because temperature rising within a certain range can increases the degree of starch swelling in water, thus ensure the reaction in the homogeneous and be propitious to disperse initiator and monomer. When the temperature rose exceeds 65˚C, the chain termination reaction rate increased, which lead to lower grafting yield, so the water content in filter cake was higher.

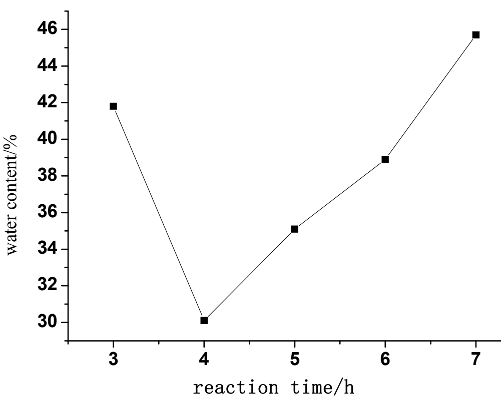


Figure 4. The effect of reaction time on water content in filter cake

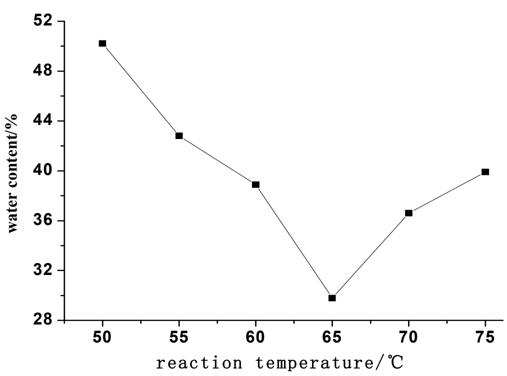


Figure 5. The effect of reaction temperature on water content in filter cake

3.2 Analysis of FTIR

Figure 6 and **Figure 7** are respectively FTIR spectra of starch and copolymer flocculant. As can be seen from the **Figure 6**, the peak of IR spectra of -OH symmetric stretching vibration in starch glucose unit appeared at 3440 cm^{-1} and 3442 cm^{-1}. From **Figure 7**, we can know the peak of IR spectra of C=O stretching vibration and $-NH_2$, $-CH_2$ stretching vibration in copolymer flocculant appeared respectively at 1670 cm^{-1}, 3198 cm^{-1}, 1027 cm^{-1}. There be should have two absorption peak at 3198 cm^{-1}, but it overlapped with the strong broad hydroxyl peak of starch, so there was only a single peak. The absorption peak appeared at 1618 cm^{-1} was the $-NH_2$ bending vibration characteristic peaks. So, there must have some structural units of AM and DMC in the starch- based cation copolymer flocculant.

3.3 Flocculent Effect

From **Figure 8** we can see that adding the same amount of flocculant, the flocculent effect of organic flocculants was better than that of inorganic coagulant, but the results are not satisfactory, the water content in filter cake

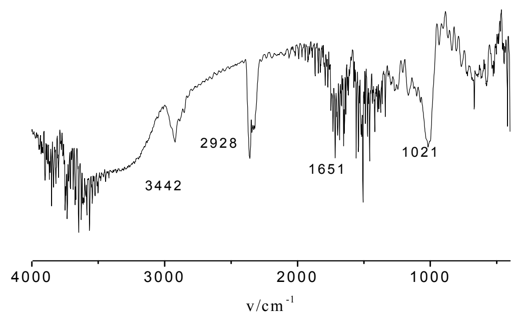


Figure 6. FTIR spectra of corn starch

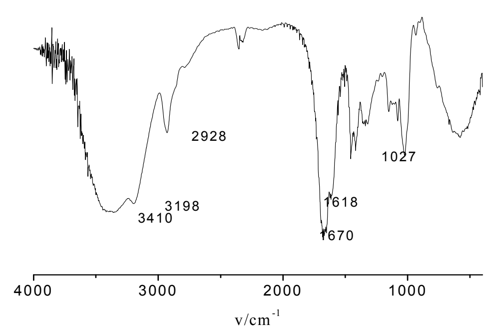
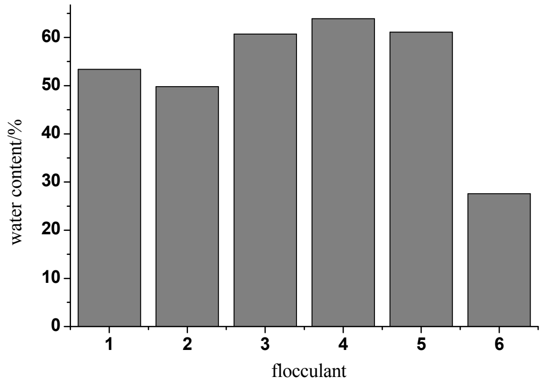


Figure 7. FTIR spectra of starch-based cation copolymer flocculant



1—Non-ionic polyacrylamide; 2—Cationic polyacrylamide; 3—Anionic polyacrylamide; 4—Polymerization ferric sulphate; 5—Polymerization aluminum sulfate; 6—Starch-based cation copolymer

Figure 8. Floccuent effect of some flocculant

was more than 50%. From **Figure 8**, the flocculent effect of the starch-based cation copolymer flocculant was significantly better than that of the other coagulant in market, water content of waste drilling mud after treated rate was 27.6%.

4. Conclusions

Starch, 2-Trimethylammonium ethyl methacrylate chloride (DMC) and acrylamide (AM) used as raw material and potassium persulfate as initiator to prepare a starch-based cation copolymer flocculant. For high-density waste drilling mud, the flocculent effect of the starch-based cation copolymer flocculant flocculation was significantly better than that of the other coagulant in market.

5. Acknowledgements

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