Preparation and Performance Analysis of Lignocellulose Water Retention Agent and Combination with Coal Gangue Ceramsite

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Abstract. Environmental friendly water retention agent has been widely used in agriculture, since its ability to absorb water, hold in water, resist salt. In this study, the water retention agent was polymerized with using wood cellulose as raw material, acrylamide as monomer, N, N - methylene double acrylamide as crosslinking agent, ammonium persulfate as the initiator. The optimized technological conditions was obtained by the orthogonal experiments: the quality ratio of cellulose and acrylamide was in 1:6, ammonium persulfate was 1.5 wt%(of the total amount of cellulose and monomer), N, N - methylene double acrylamide 0.25 wt%(of the total amount of cellulose and monomer). The maximum water absorbency of water retention agent was 330.07g/g in distilled water and 117.48g/g in 0.9 wt% KCl solution. On the basis of this, using water retention agent as the coating for coal gangue ceramsite, and the maximum water absorbency of water retention agent was 332.15g/g in distilled water and 118.91g/g in 0.9wt% KCl solution. The results show that adopting above process not only can obtain good water retention agent, but also can enhance the water retention and salt resistance by using with ceramsite.

1. Introduction
Lignocellulose is plentiful in nature and is one of the most promising renewable resources[1]. The structure of lignocellulose is similar to super absorbent resin, both of them are natural reticular formation containing a large number of hydrophilic group[2]. Using lignocellulose as raw material to carry on the graft polymerization reaction to prepara super absorbent resin, will greatly increase the additional value. It’s one of the important way to use lignocellulose. At the same time, comparing to other raw materials of water retention agent ,such as starch, protein, etc., lignocellulose can widely replace chemical raw materials and will not affect the human food supply[3]. At present, the research on the super absorbent resin of cellulose has been paid attention to, but the research on the salt resistance is not sufficient. In the western regions of China, such as Qinghai’s ecological environment is fragile because the salination in some areas is serious, and enhancing the salt resistance of water retention agent has profound guiding significance for the improvement of saline and alkaline land[4]. This study mainly considered the following factors:the quality ratio of cellulose and acrylamide, the dosage of initiator, the dosage of crosslinking agent[5]. Experimenting with each influence gradually and on that basis designing orthogonal experiment to obtain the optimal technological condition. Coal gangue ceramsite is beneficial to loose soil and has absorbability[6]. Using it with water retention agent in agriculture soil, not only can improve soil porosity and permeability but also can take full of advantage of water retention agent absorbent and salt resistance. On the basis of preparing water
retention agent, this paper used the water retention agent as the coating for coal gangue ceramsite and research performance of them closely combined.

2. Experiment

2.1. Experimental Material
lignocellulose SD - 300; ammonium persulfate, AR; acrylamide, AR; N, N - methylene double acrylamide, AR; sodium hydroxide, AR ; absolute ethyl alcohol, AR; coal gangue ceramsite(made in our laboratory).

2.2. Preparation of Water Retention Agent
In a flask, dissolve a certain amount of cellulose in distilled water, N₂ atmosphere. Cool to 20°C, add the initiator ammonium persulphate and stir to dissolve about 5mins. Then add acrylamide and N, N - methylene double acrylamide at 70°C, N₂ atmosphere. Stir the mixture until it becomes uniform slurry. Add sodium hydroxide to hydrolyze. After the gel is formed, remove it from the reaction vessel. Then, wash it with distilled water and absolute ethyl alcohol. Dry it in a constant temperature oven. After a while, take out the product and snip into small chunks.

2.3. Combination with Coal Gangue Ceramsite
Combine water retention agent made by experiment with coal gangue ceramsites, which are about 5-7 mm in diameter and 423 kg/m³ in bulk density. Research the performance of the product after the combination.
Take a group of ceramsite, coat them with water retention agent. Ceramsites should be wrapped in resin totally and the thickness of the coating layer is about 3 mm.

2.4. Performance of Product
2.4.1. Water Absorption
Water absorption (ml/g or g/g) can be defined as the volume or mass of the liquid absorbed by the unit mass water-retaining agent in unit time.
First, cut a dry sample and weigh accurately with the analytical balance, and the mass of the dry sample was m₁(g). Then, add the sample and 300ml distilled water into 500ml beaker, mix well. Static for 24h, the water retention agent becomes hydrogel after absorbing water. At this point, use absorbent paper absorb the surface water. Then, weigh the hydrogel accurately with the analytical balance, the mass is m₂(g). Repeat three times to take an average. Thus, the water absorption rate of the sample is Q₁ (g/g). The formula of water absorption ration is following:

\[ Q_1 = \frac{(m_2 - m_1)}{m_1} \]  

2.4.2. Salt Resistance
The salt resistance of water retention agent can be defined as the ability to absorb water in saline solution. Experiment with nonelectrolyte urea and electrolyte potassium chloride to research the absorption rate respectively, experimental method is similar with the water absorption rate.
Take a polymer and weigh it accurately with the analytical balance, the mass is m₁ (g). Then place the sample in 500ml beaker and add in 300ml of 0.9%wt salt solution and mix well. Static 24h, the surface water was absorbed by absorption paper, accurately weigh the hydrogel. The mass is m₂ (g). Next, take the average of three repeated measurements. The salt absorption rate of the sample is Q₂(g/g). The calculation formula of salt resistance is:

\[ Q_2 = \frac{(m_2 - m_1)}{m_1} \]  

The salt resistance of water retention agent is usually researched by using salt solution which can ionize a valence ion[7], such as KCl, which is also a kind of common potassium fertilizer. Therefore, the salt absorption rate in the results discussion and analysis was measured in 0.9wt% KCl solution. The salt absorption rate in urea solution was studied in the combination of water retention agent and ceramsite.
3. Results Analysis and Discussion

3.1. Effect of the Mass Ratio of Cellulose and Monomer
The biggest factor is the mass ratio of cellulose and acrylamide[8]. We chose the mass ratio: 1:3, 1:4.5, 1:6, 1:8, 1:10, 1:12. Experimental conditions: ammonium persulfate 2.5 wt% (of the total amount of cellulose and monomer), N, N-methylene double acrylamide 0.375 wt% (of the total amount of cellulose and monomer).

Figure 1. The effect of the mass ratio of cellulose and monomer on water absorption and salt resistance.

Figure 1 shows that when the mass ratio of cellulose and monomer is in the range of 1:3 to 1:6, the absorption rate of products increases with the increase of mass ratio. Once ratio exceed 1:6, the absorption rate of the product decreases with the increase of mass ratio. Since acrylamide is nonelectrolyte, it hardly disassociates into ions in water[9]. With the increase of mass ratio, the number of grafting point increases, the absorbent and salt resistance also increase. But when ratio exceed 1:6, the resin is self-linking highly, and the grafting rate decreases, so the absorption rate decreases[10]. Thus, when the mass ratio of cellulose and monomer is 1:6, water retention agent has the maximum absorption rate.

3.2. Effect of Ammonium Persulphate
The mass ratio of cellulose and monomer is 1:6, N, N-methylene double acrylamide 0.375% (of the total amount of cellulose and monomer). Experimental conditions keep unchanged, change ammonium persulfate mass, the results are shown in Figure 2.
The effect of ammonium persulphate on water absorption and salt resistance.

The reason why initiator can accelerate the reaction rate is producing new free radical[11]. From Figure 2: the evolution of the effect can be broadly divided into three phases.

When ammonium persulfate dosage below 1.5 wt% of the total amount of cellulose and monomer, product absorbability decreases with the increase of ammonium persulfate dosage.

When ammonium persulfate dosage in the range of 1.5 wt% to 2.5wt%, product absorbability increases with the increase of ammonium persulfate dosage.

When ammonium persulfate dosage exceed 2.5 wt%, product absorbability decreases with the increase of ammonium persulfate dosage.

Figure. 2 shows that when ammonium persulfate dosage is 2.5 wt%, water retention agent has maximum absorption rate. Under low dosage, initiator produces new free radical at a slower rate. So water retaining agent has slower aggregation rate, small crosslinking degree, poor absorbability[12]. As ammonium persulfate dosage increases, formation rate of free radical speeds up. It will accelerarate aggregation rate, increase crosslinking degree, also increase product absorbability. However, when dosage exceeds the limits, although add moreinitiator will accelerarate formation rate of free radical and aggregation rate, chain termination reaction rate speeds up, add percent of oligome, decrease product absorbability totally[13].

3.3. Effect of N, N - Methylene Double Acrylamide
Experimental conditions: the mass ratio of cellulose and monomer is 1:6, ammonium persulfate 2.5%(of the total amount of cellulose and monomer). Experimental conditions keep unchanged, change cross linking mass, the results are shown in Figure 3.
Figure 3. The effect of N, N - methylene double acrylamide on water absorption and salt resistance.

With increase of crosslinking agent dosage, product water absorption and salt absorption increase first and then decrease. Because in grafting reaction, the function of crosslinking agent are forming water uptake networks by cross-linking absorbent groups and make lignocellulose framework stronger to improve product absorbability[14]. When crosslinking agent dosage is too little, resin density lower, the three-dimensional net structure of polymer bigger, more dissolvable parts, higher water-solubility, so product absorbability is poor[15]. On the contrary, when crosslinking agent dosage is too much, the net-structure of polymer has more cross-links. However, crosslinking points associating with one another strongly will limit the space, and it would be bad for water retention agent swelling in water, so product absorbability is poor as well[16]. In conclusion, when N, N - methylene double acrylamide dosage is 0.25 wt%, water retention agent has maximum absorption rate.

### 3.4. The Optimized Technological Conditions

By analyzing the mass ratio of the monomer, the dosage of initiator and crosslinking agent, we get that when the mass ratio of cellulose and monomer is 1:6, ammonium persulfate 2.5 wt%, N, N - methylene double acrylamide 0.375 wt%, water retention agent has slightly higher absorption rate. On this basis, run the optimum conditions to obtain the optimized technological conditions. Factor levels are shown in Table 1.

| Table 1. Factor levels. |
|-------------------------|
| Factor level | the mass ratio of the monomer | Ammonium persulfate dosage % | N,N-methylene double acrylamide dosage % |
| Level 1 | 1:5.5 | 2.25 | 0.25 |
| Level 2 | 1:6 | 2.5 | 0.3125 |
| Level 3 | 1:6.5 | 2.75 | 0.375 |

Through orthogonal experiment, we obtained the process parameters and the optimal formula. Experimental conditions: the mass ratio of cellulose and monomer is 1:6, ammonium persulfate 2.25%, N, N - methylene double acrylamide 0.375%. In this case, water retention agent has maximum absorption rate and the maximum water absorbency of water retention agent was 332.15g/g in distilled water and 118.91g/g in 0.9wt% KCl solution. The performance of water retention agent made in experiment is better than other water retention agent with cellulose reported in literatures[17].
3.5. The Absorbability after Water Retention Agent and Ceramsite Combining

Take water retention agent, water retention agent used with ceramsite, measure water absorption rate and salt absorption rate(in 0.9 wt% urea solution and 0.9 wt% KCl solution). Results are shown in Table 2. Analyzing Table 2, water retention agent used with ceramsite has no influence on water absorption rate and salt absorption rate, nonelectrolyte urea has little effect on absorbability.

| Absorb media (0.9%wt salt solution) | distilled water | urea | KCl |
|-------------------------------------|----------------|------|-----|
| absorbability (g/g)                 | 330.07         | 310.16 | 117.48 |
| absorbability combined with ceramsite (g/g) | 332.15 | 458.54 | 118.91 |

Based on the theory of Flory-Huggins water uptake model[18], water retention agent absorbability relates to ion concentration of electrolyte solution. Urea is nonelectrolyte, exists as molecules in water, can not dissociate into ions. So it has little affect on absorbability. On the contrary, potassium chloride dissociates in water, absorbability declines precipitously. But in this experiment, water retention agent is good in saltresistance, leading to its strong applied value in saline soils. The existing literatures have not reported cellulose water retention agent absorbability in 0.9 wt% KCl solution.

4. Conclusion

This paper synthesized a super absorbent resin by using a lignocellulose SD-300, and measured its water absorption ratio and the salinity resistance. The optimized technological conditions are obtained by analyzing the experimental results: When the mass ratio of lignocellulose and monomer is 1:6, the dosage of initiator is 2.25%, the dosage of crosslinking agent is 0.375%, water retention agent can reach 330.07 g/g in distilled water and 117.48 g/g in 0.9 wt% KCl solution. After combining with coal ceramsite, the water absorption rate is 332.15 g/g, and the salt absorption rate is 118.91 g/g. It can be seen that the water retention agent absorbent capacity and salt tolerance are not affected after combining, using them together is promising in soil improvement.

5. References

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