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Effects of Coking Wastewater on Preparation of Coal Pitch Water Slurry

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The coal pitch water slurry was prepared by coal pitch powder, dispersants and two different kinds of coking wastewater. The apparent viscosity, rheological behavior and stability of the coal pitch water slurry were investigated. The results indicated that both the two kinds of coking wastewater could be used to prepare coal pitch water slurry. Moreover, the adsorption of dispersants and zeta potential on coal pitch's surface were also studied. The adsorption of dispersants and the zeta potential increased rapidly at first, then reached the balance and declined slightly at the last with the increasing of solutions' concentrations. The adsorption amount and the zeta potential reached the maximum with dispersants dosage of 1200 mg/L.

Keywords: Coal pitch, Coal pitch water slurry, Coking wastewater, Rheology, Zeta potential.

INTRODUCTION

The coal pitch is the dominant product in the processing of coking. The research and application of coal pitch have already referred to many fields such as carbon materials, electrode materials, impregnating pitch, needle coke, carbon fibers, paving and building materials[1-4]. However, vast amounts of coal pitch is utilized insufficiently and this problem is getting worse with the development of coal chemical industry. Therefore, how to make full use of the coal pitch is increasingly important.

Coking wastewater is a kind of persistence organic, produced during the high temperature distillation, gas purification and chemical products refined process of coal. The coking wastewater has a complex composition with high concentration and toxicity. It has high concentrations of phenol, polycyclic aromatic hydrocarbons and heterocyclic compound containing oxygen, sulfur and nitrogen, *etc.* and also contains a lot of anion such as cyanide, sulfur cyanogen root and cationic inorganic compounds such as silicon, calcium, iron, magnesium and sodium. The excessive emission of coking wastewater is hazardous to human beings, aquatic products and crops. At present, the coking wastewater can not have an effective governance due to the imperfect technology and it cannot be discharged directly before treatment[5,6]. Therefore, the utilization research of the coking wastewater is significant. An effective method to solve this problem is using the coking wastewater to prepare the coal water slurry (CWS)[7,8].

In this work, preparation of the coal pitch water slurry (CPWS) with coking wastewater before biochemical treatment (W1) and coking wastewater after biochemical treatment (W2) was studied, based on the preparation process of coal pitch water slurry[9,10].

EXPERIMENTAL

The softening point of coal pitch was measured by ring-ball method. The elemental analysis was done by Elemental analyzer produced by Elementar company in Germany. Coal pitch is middle temperature coal pitch whose softening point is 90 °C. The elemental analysis are showed as Table-1.

TABLE-1
ELEMENTAL ANALYSIS OF COAL PITCH

Numbers	Element contents (%)			
	C	H	N	O
1	93.12	0.97	4.52	1.39
2	93.05	0.94	4.50	1.51
Average value	93.08	0.96	4.51	1.45

Coal pitch lump was frozen at -25 °C for 24 h, then it was pulverized for 1 s with high-speed disintegrating machine, at last the powder was sieved with 60 mesh standard sieves. Particle size distribution of coal pitch powder was examined by HORIBA Ltd. LA-300 particle size distribution analyzer. The results are showed in the Fig. 1. The particle size of coal pitch powder belong to bipeak grainsize distribution.

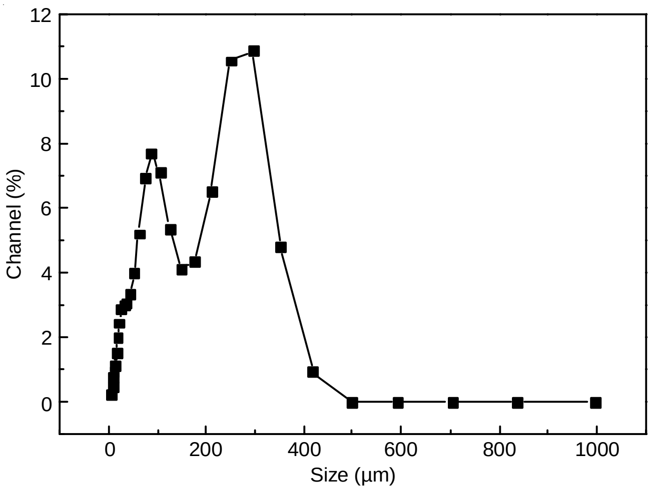

Fig. 1. Granularity distribution of coal pitch powder

The main chemical properties of the two kind of coking water W1 and W2,presented in Table-2. The dispersants used in this research were JL-C01 emulsifiers and cationic surfactants with complex structures, industrial products, were bought from Tian Long Chemical Industry Co., Ltd., Luo He city, China.

TABLE-2
MAIN CHEMICAL PROPERTIES OF COKING WASTEWATER

Coking wastewater	pH	COD (mg/L)	Volatile phenol (mg/L)	NH_4^+-N (mg/L)	Cyanide (mg/L)	Oil (mg/L)
W1	6.51	640.0	65.0	70.0	13.0	35.6
W2	5.47	150.0	0.5	5.0	0.5	10.0

Coal pitch slurries preparation: Coal pitch water slurry was prepared by adding certain dispersant to quantitative coking wastewater, then stirring under the speed of 3000 rpm till the dispersant was dissolved. Coal pitch water slurry was ready after shaking well. The slurry ability and rheological property were tested by the NXS-4C type viscosimeter. The biggest slurry concentration is calculated under 20 °C, when shear rate is 100 s^{-1}. The apparent viscosity is less than 1200 mPa·s, rheological property is judge by the trend of apparent viscosity changing with shear rate. The stability was examined by the method of inserting-stick observation.

Adsorption of dispersing agent in coking wastewater on the coal pitch surface: The solutions with dispersant agent of different concentration (0, 200, 400, 600, 800, 1000, 1200, 1600, 2000 mg/L) were prepared with two kinds of wastewater (W1, W2), 2.0 g coal pitch powder was added respectively to 100 mL solution prepared with different concentration, oscillating for 24 h at constant temperature of 25 °C in order to achieve adsorption balance. The upper clear liquid was reserved by centrifugal separation for adsorption measurement using TU-1901 ultraviolet spectrophotometer.

1 mL Stay test solution was added in the 25 mL volumetric flask and then 1 mL OP solution whose mass fraction was 0.5 % and 5 mL 1.6×10^{-4} mol/L BTB solution and 2.5 mL pH = 7.7 buffer solution (made with 0.2 mol/L monopotassium phosphate solution and 0.2 mol/L disodium phosphate solution mixed in a certain proportion) were joined in sequence. Then coking wastewater was added in the 25 mL volumetric flask to dilute and shook it well. The absorbance of the Stay test solution was measured with coking wastewater as reference.

The adsorbance of dispersing agent in coking wastewater on the coal pitch surface was calculated using the formula as follow:

$$\Gamma = (C_0 - C)V/G$$

where: Γ = the adsorbance of certain concentration (mg, dispersant/g, coal pitch); C = the equilibrium concentration of dispersing agent (mg/L); C_0 = the Primitive concentration of dispersing agent (mg/L); V = the bulk of dispersant solutions (L); G = the weight of coal pitch powder (g).

Zeta potential of coal pitch surface: The solutions with dispersant agent of different concentration (0, 200, 400, 600, 800, 1000, 1200, 1600, 2000 mg/L) were prepared with two kinds of wastewater (W1, W2). 2 g coal pitch powder was added respectively to 100 mL solution prepared with different concentration, oscillating for 24 h at constant temperature of 25 °C in order to achieve adsorption balance. The zeta potential was measured by JS94H electrophoresis apparatus.

RESULTS AND DISCUSSION

Study on the viscosity of coal pitch water slurry: The coal pitch water slurry (CPWS) of different concentrations was prepared with the two kinds of coking wastewater (W1, W2). Effects of dispersants on the viscosity were investigated. The results were reported in Fig. 2.

As seen in Fig. 2, the viscosity of coal pitch water slurry increased with the growing of concentration. The lower viscosity of coal pitch water slurry was that prepared by W1. Slurries prepared by W1 and W2 could be obtained at a concentration of 70 %, with the dosages of dispersants set in 0.4, 0.6, 0.8 and 1.0 %.

Rheological behaviour of coal pitch water slurry: The rheological behaviour of coal pitch water slurry prepared by W1, W2 with the dosages of dispersants set in 0.4, 0.6, 0.8 and 1.0 % were shown in Figs. 3 and 4. As seen in the figures, the apparent viscosity of coal pitch water slurry prepared by W1, W2 decreased with the growing of shear rate and slurry concentration. It indicated that the coal pitch water slurry prepared by wastewater was pseudo-plastic fluid. The slurries could be obtained at 70 % concentration with the dosages of dispersants set in 0.4, 0.6, 0.8 and 1.0 %. The rheological behaviour of coal pitch water slurry prepared by W1 is better than W2.

Study on the stability of coal pitch water slurry: The stability of coal pitch water slurry was investigated by 'rod-insertion' method, putting a long rod into the slurries to test whether it was hard. As shown in Tables 3 and 4, the stability of coal pitch water slurry prepared by W1, W2 become weaker with time. Moreover, the stability declined with the increasing concentration at the same dosage of dispersants. The dosages of dispersants had nothing to do with the stability. However, the stability increased with the growing of dispersants' dosages at a concentration of 70 %. The coal pitch water slurry prepared by two different kinds of coking wastewater could be stable for as long as 30 days, while the coal pitch water slurry prepared by W1 was more stable than that by W2.

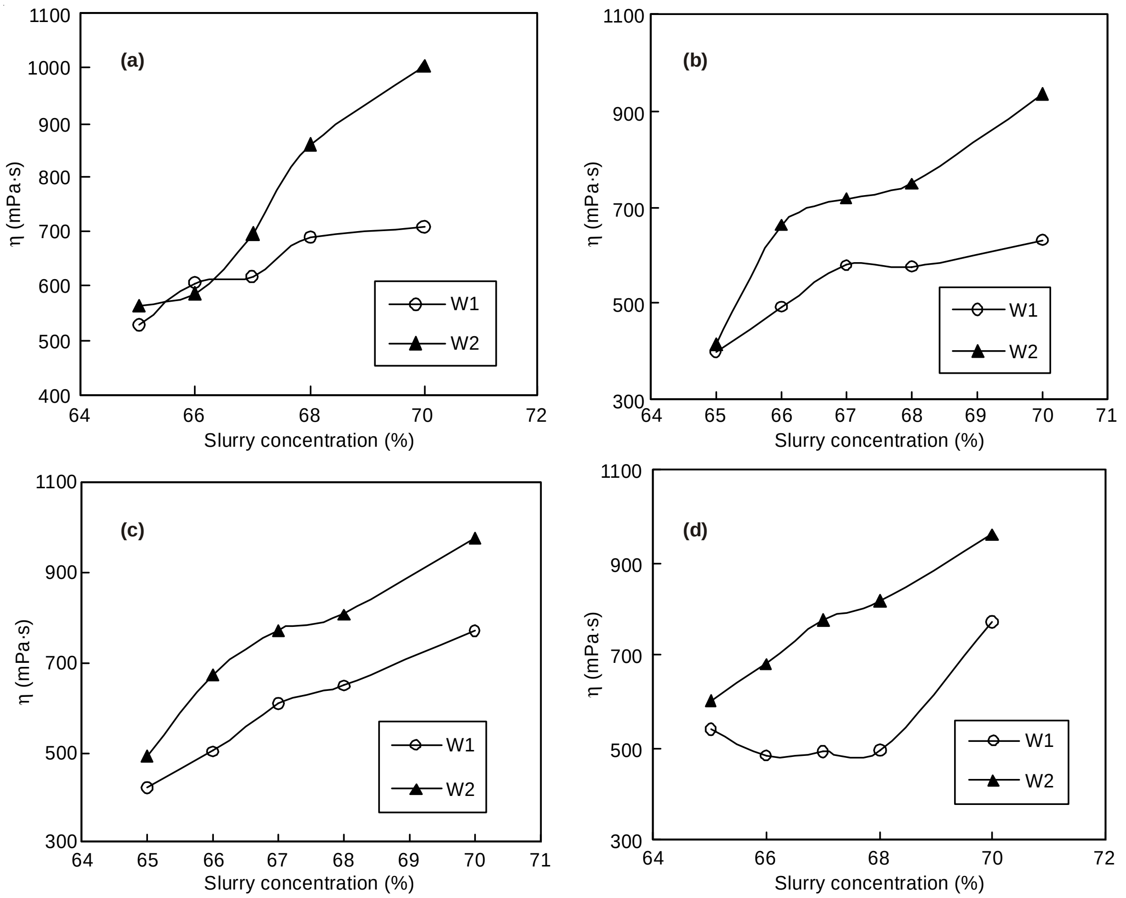

Fig. 2. Influence of coal pitch water slurry ability by slurries concentration and dispersant dosage. The dispersant dosages is (a) 0.4 %, (b) 0.6 %, (c) 0.8 %, (d) 1.0 %

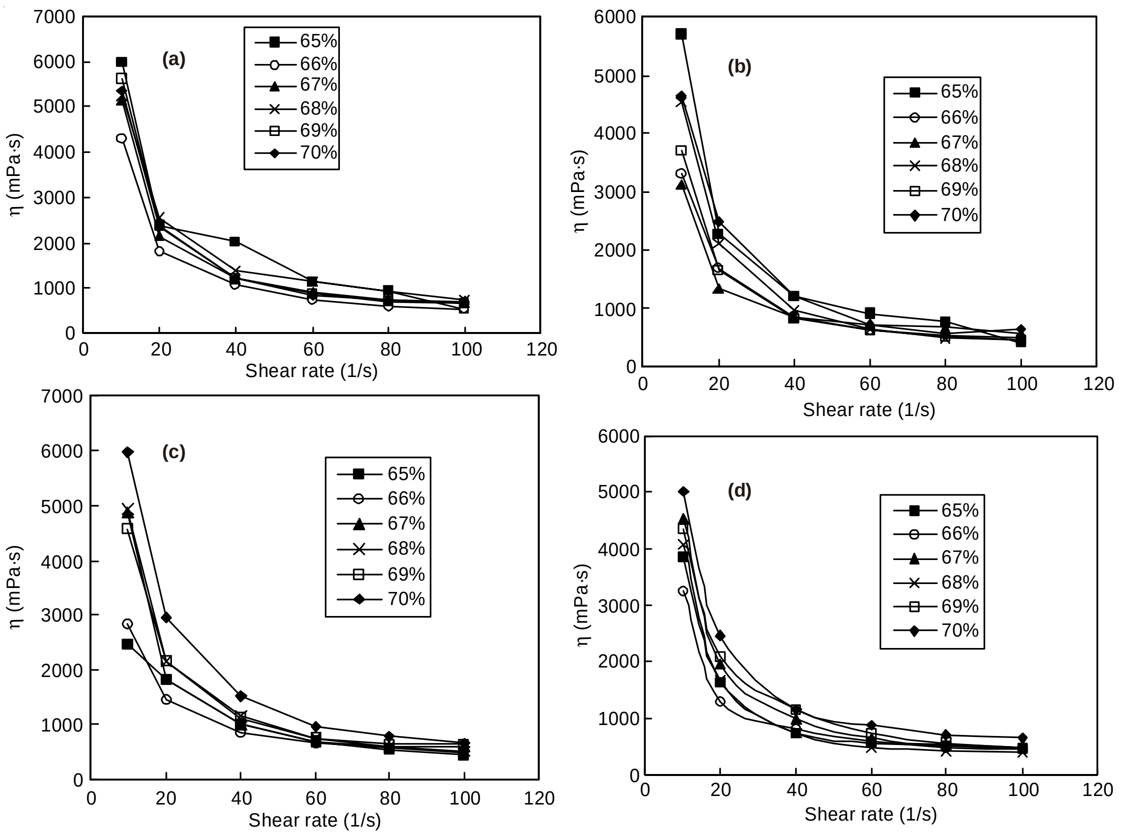

Fig. 3. Effect of the slurries concentration on rheology of coal pitch water slurry that was prepared by W1. The dispersant dosages is (a) 0.4 %, (b) 0.6 %, (c) 0.8 %, (d) 1.0 %

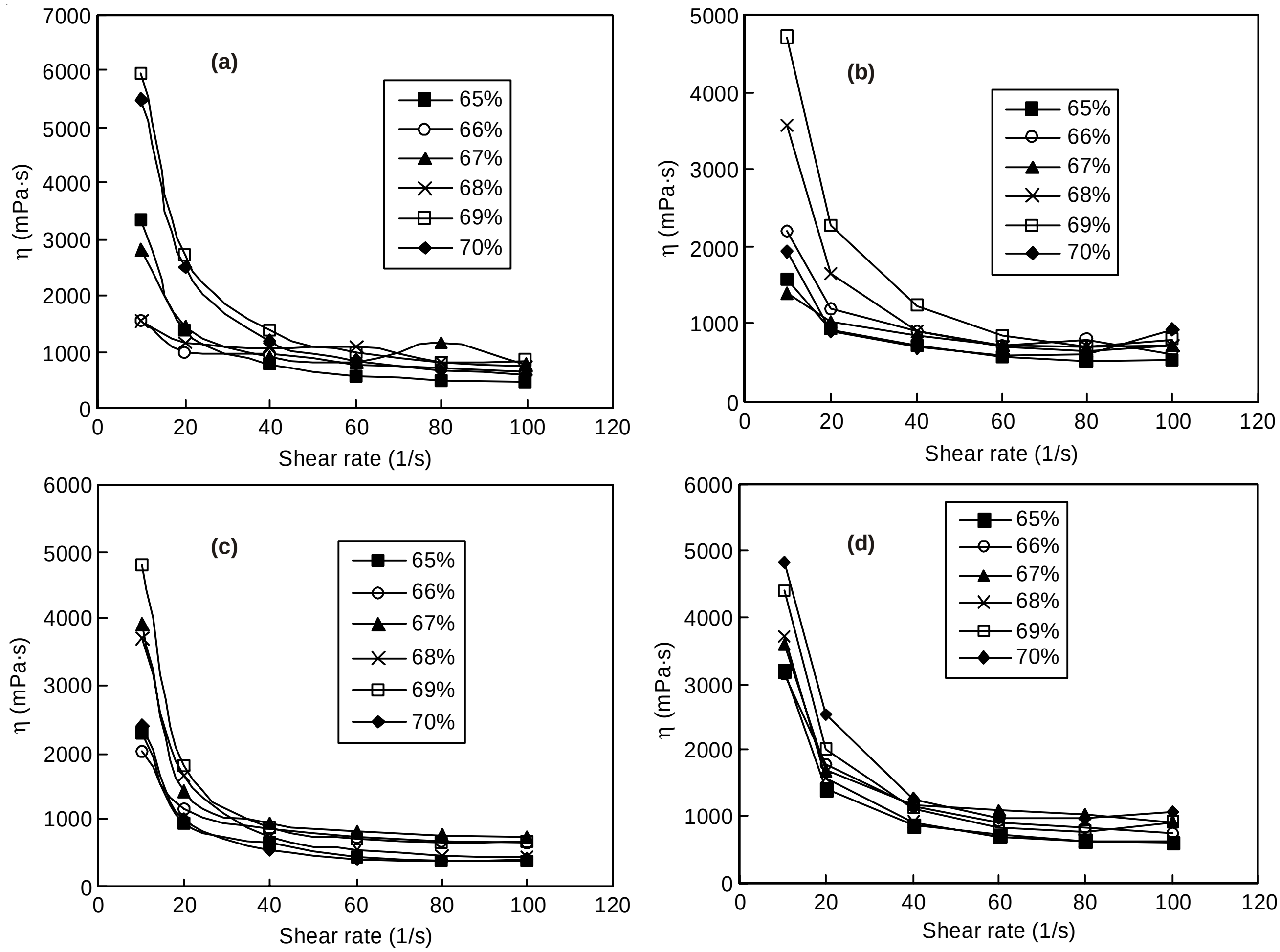

Fig. 4. Effect of the slurries concentration on rheology of coal pitch water slurry that was prepared by W2. The dispersant dosages is (a) 0.4 %, (b) 0.6 %, (c) 0.8 %, (d) 1.0 %

TABLE-3
STABILITY OF COAL PITCH WATER SLURRY BY W1

Dispersant (%)	Stability (days)				
	65	66	67	68	70
	Slurry concentration (%)				
0.4	33	30	32	28	19
0.6	34	35	29	29	18
0.8	34	28	33	30	25
1.0	33	35	32	23	27

TABLE-4
STABILITY OF COAL PITCH WATER SLURRY BY W2

Dispersant (%)	Stability (days)				
	65	66	67	68	70
	Slurry concentration (%)				
0.4	28	30	29	27	15
0.6	29	29	29	26	14
0.8	30	27	31	27	24
1.0	31	29	32	24	23

Adsorption of dispersants on coal pitch: The coal pitch powder was added into the solutions of dispersants at different concentrations, which were prepared by two kinds of coking wastewater (W1, W2). And the adsorption of dispersants on the coal pitch surface was determined when the adsorption reached balance. The results were shown in Fig. 5. The results indicated that the adsorption capacity of dispersants increased with the growing concentration in coking wastewater. The maximum adsorption capacity was obtained at the concentration of dispersants about 1200 mg/L. The interaction between dispersants and coal pitch particles in aqueous solution was a monolayer adsorption of Langmuir reaction when saturated and multi-layer adsorption occurred at last. The tight double electrical layer structure could not be formed on the surface of particles before saturated and monolayer adsorption of Langmuir took place. Therefore, the interactional repulsive force among particles was so weak that cohesion was more likely to happen when the particle collide with one another, leading to poor dispersed status and liquidity of the coal pitch water slurry. When saturated and monolayer adsorption of Langmuir occurred, it formed the tight double electrical layer structure on the surface of particles. Moreover, the interactional repulsive force among particles reached a maximum, the cohesion among particles was less likely to happen. The dispersing of coal pitch in water and liquidity of coal pitch water slurry became well. The surface of coal pitch was multihole. The adsorption of dispersants not only occurred on the surface of solid, but also in the holes of particles.

Zeta potential of coal pitch's surface: The coal pitch powder was added into the solutions of dispersants at different concentrations. The zeta potential of coal pitch's surface

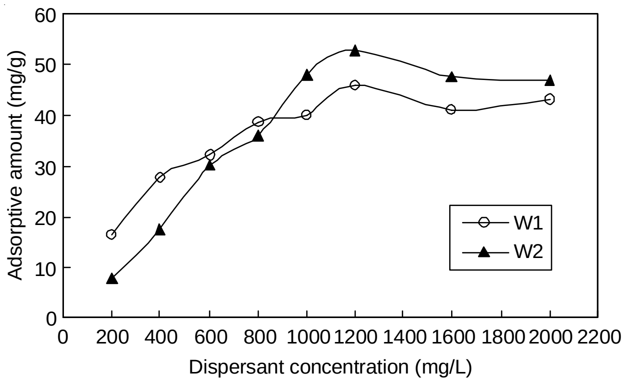

Fig. 5. Adsorption of dispersing agent in coking wastewater on the coal pitch water slurry

was investigated by miniature electrophoresis apparatus, as presented in Fig. 6. The results showed that changing laws of zeta potential in different coking wastewater were coincident. The zeta potential increased with the growing concentration. The surface of coal pitch powder was electronegative in water without dispersants added. The adsorption of dispersants and the zeta potential increased rapidly, reached the balance and declined slightly at the last with the increasing of solutions' concentrations. The zeta potential reached a maximum when the concentration of dispersants were 1200 mg/L. This value was consistent with the adsorption. The reason could be that as the increasing of dosages, more and more dispersants were adsorbed on the surface of coal pitch to overcome electrostatic repulsion, so the zeta potential increased. When the adsorption of dispersants became saturation, the zeta potential reached a maximum. Multilayer adsorption would occur with further adding of dispersants. At the same time, the zeta potential decreased a little, which was consistent with that of coal water slurry.

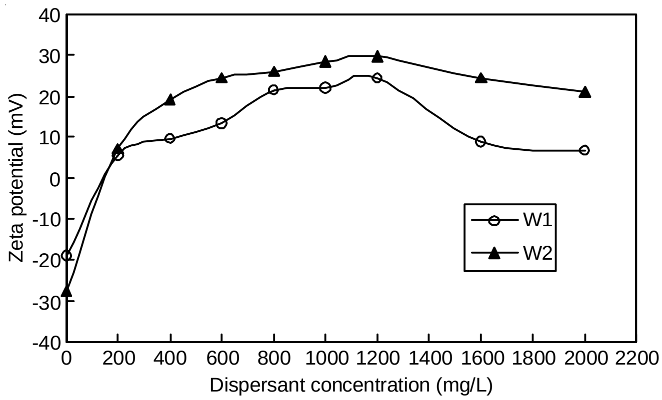

Fig. 6. Zeta potential of coal pitch surface in different coking wastewater

Conclusion

When the dispersants were to maintain a constant dose, the viscosity of coal pitch water slurry increased with the growing concentration. The coal pitch water slurry prepared by W2 has the lower viscosity. The apparent viscosity of coal pitch water slurry prepared by W1, W2 declined with the increasing shear rate. In the same shear rate, the apparent viscosity increased with the growing concentration. This indicated that the coal pitch wastewater slurry was pseudo-plastic fluid. And the coal pitch water slurry prepared by W1 was better than W2. The stabilities of coal pitch water slurry prepared by W1, W2 decreased with time. At the same dosages of dispersants, the stabilities decreased with the growing concentration. The stability of coal pitch water slurry prepared by W1 was better than W2. The adsorption of dispersants and the zeta potential on the coal pitch increased with the growing dispersants' concentrations and reached the maximum at 1200 mg/L.

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