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The Effect of Water-Soluble Polymers on the Stability and Rheological Properties of Suspensions of Fibrous Activated Charcoal

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Abstract—The stability and rheological characteristics of polymer-containing aqueous suspensions of fibrous activated charcoal are determined. It is shown that the improved stability of suspensions is observed in the presence of carboxymethyl cellulose, oxypropyl methyl cellulose, polyvinylpyrrolidone, and a new water-soluble cellulose derivative, whereas the presence of polyacrylamide, poly(acrylic acid), poly(vinyl alcohol), and starch leads to the formation of unstable suspensions having a broad particle size distribution. A correlation between the concentration of dispersed-phase particles corresponding to the transition to non-Newtonian flow and the characteristics of suspension stability (such as the rate of sedimentation, the volume of the sediment, and the particle size distribution) is established. It is suggested that the high degree of charcoal particle surface hydrophilization by polyvinylpyrrolidone and by the water-soluble cellulose derivative is mainly responsible for the stability of the modified suspensions.

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INTRODUCTION

Activated charcoals as nonspecific enterosorbents are widely used in medicine for removal of endo- and exogenous toxins and metabolic wastes from the organism, for correction of dyslipidemia, etc. [1]. Among these substances, improved physicomechanical, structural, and adsorption properties are characteristic of fibrous activated charcoals, which are the products of carbonization and subsequent activation of hydrated cellulose materials (fibers, fabrics, and nonwoven materials). Such adsorbents have been approved for use in medicine in the form of fabrics or powders prepared by their grinding.

In literature, publications on the properties of dispersions of fibrous activated charcoal (FAC) are absent. The aim of this work was to study the stability and rheological characteristics of aqueous dispersions of FAC modified by various polymers. This work can be helpful because all medicinal forms of activated charcoal (powders, capsules, tablets) form a charcoal suspension within the gastrointestinal tract of a patient, and the therapeutic effect of the enterosorbent depends on the rate of formation, dispersity, stability, and fluidity of this suspension. In this case, the suspension properties are determined not only by colloidal characteristics of charcoal particles, but also, to a great extent, by the nature of the water-soluble polymer that is used as the binder for tablets or as the capsule shell material and adsorbed on the surface of charcoal particles.

EXPERIMENTAL

The FAC was used in the form of powder of grade AUT-MI (finely dispersed activated carbon fabric, FDACF). The medicinal products based on FDACF were prepared under laboratory conditions as granules and tablets. For preparing the granulate, the aqueous solution of the polymer was added to the corresponding weighed portion of the charcoal powder and then stirred thoroughly. The resulting mixture was dried or first pressed into tablets and then dried. As the water-soluble polymers, we used vinyl polymers, such as poly(vinyl alcohol) (PVA), polyacrylamide (PAA), poly(acrylic acid) (PAAc), and polyvinylpyrrolidone (PVP) with molecular masses M_η equal to 4.4×10^6, 4×10^6, 5×10^5, and 3×10^5, respectively; cellulose derivatives, such as oxypropyl methyl cellulose (OPMC), carboxymethyl cellulose (Na-CMC), and a new water-soluble cellulose derivative (WSCD)[1] with M_η values equal to 5.5×10^5, 1.35×10^5, and 3.4×10^4, respectively; and soluble starch. The polymer content in the granulates and tablets was $(1–18) \times 10^{-4}$ mol units per gram of charcoal and corresponded to the formation of solutions with equal viscosities.

Aqueous suspensions of charcoal with the concentration of the dispersed phase 5–35 wt % were prepared in equal times and at equal intensities of stirring. Sedimentation analysis of the 5% suspensions was per-

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[1] The WSCD was synthesized at the Laboratory of Cellulose Solutions of the Research Institute of Physicochemical Problems, Belarussian State University.

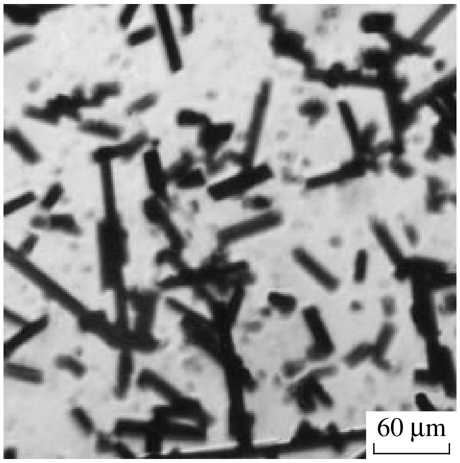

Fig. 1. Micrograph of FDACF particles.

formed by the method described in [2] on a Figurovskii sedimentometer [3]. In the version of sedimentation analysis used here, the *n* values (the numbers of microscope graduation marks) are equivalent to the weight of sedimented particles and the radii of anisometric FAC particles are effective, i.e., correspond to the radii of spherical particles settled with the same velocity.

To determine the volumes of sediments of the 5% aqueous suspensions, graduated tubes (1 cm in diameter and 30 cm in height) with ground glass stoppers were used. The suspension volume was 25 cm^3; the height of the suspension column was 25 cm. The volume of the sediments was determined visually after 30 days and the concentrations of the particle fractions contained in 5 cm^3 in the upper and lower (bottom) parts of the tube were determined by the pipette method [4]. The pattern of charcoal particle distribution in the two-phase water–trichloromethane system, which determines their hydrophilic–liphophilic properties, was estimated according to [5].

Rheological measurements of 5–35% suspensions were performed on a Rheotest-2 rheoviscometer equipped with a cylinder–cylinder measuring unit at shear stresses ranging from 1 to 200 Pa.

RESULTS AND DISCUSSION

The FAC powder in question consists of anisometric particles (Fig. 1) and, in spite of its fairly high hydrophilicity (the degree of swelling in water 50–55%), forms aqueous suspensions that are unstable with respect to aggregation [5].

Figure 2 shows that the sedimentation curves of aqueous suspensions of FAC modified by polymers (curves *2–7*) are different from the curve of the initial charcoal (curve *1*): they have a larger slope of the initial portions, i.e., lower rate of the sediment accumulation, and a lower weight of particles completely sedimented during the analysis. In this case, the minimum weight of sediments was observed for PAA and PVA (curves *6* and *7*). This can be explained by the fact that FDACF suspensions modified by the aforementioned polymers are unstable with respect to sedimentation and the majority of particles exceeding 50 μm in size sediment very fast (before the onset of the system monitoring). Thus, the resultant curves of sediment accumulation

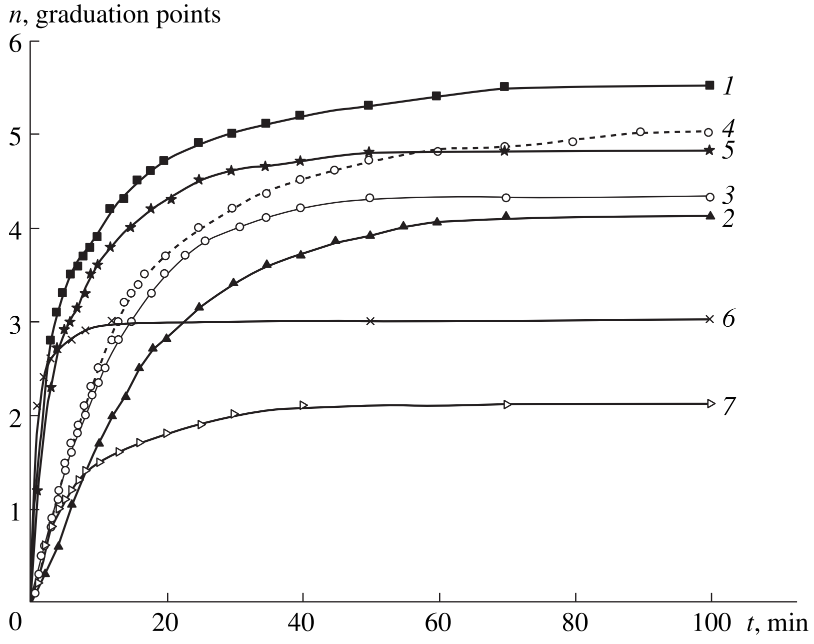

Fig. 2. Sedimentation curves for aqueous suspensions of the (*1*) initial FDACF and the same material modified by (*2*) WSCD, (*3*) Na-CMC, (*4*) OPMC, (*5*) starch, (*6*) PAA, and (*7*) PVA.

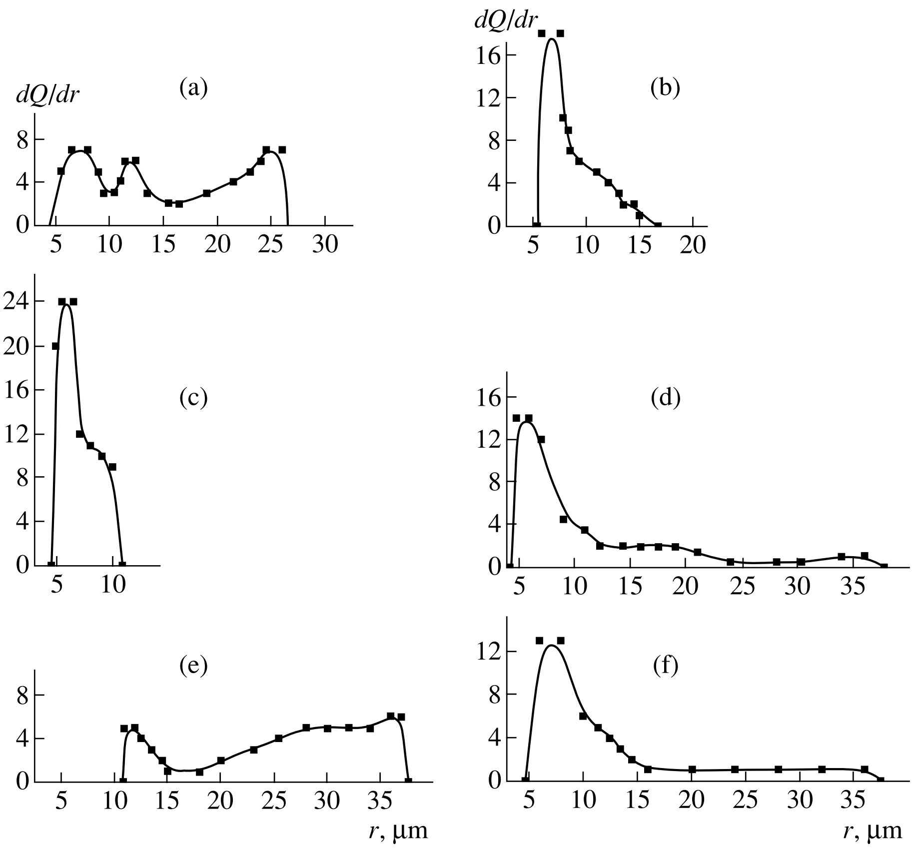

Fig. 3. Differential particle size distributions for suspensions of (a) the initial FDACF and the same material modified by (b) Na-CMC, (c) WSCD, (d) PVP, (e) PAA, and (f) PAAc.

reflect sedimentation of residual particles with a broader particle size distribution compared to particles of the initial charcoal (Figs. 3a, 3e). At the same time, a decrease in the amount of sedimented particles compared to the initial charcoal suspension was also observed for the most stable suspension, formed by charcoal in the presence of WSCD (Fig. 2, curve *2*). In this case, the decrease in the weight of particles sedimented during the analysis is not due to ultrafast sedimentation but rather to the appearance of a fraction of ultradispersed particles ($r \leq 8 \times 10^{-7}$ m), which remain suspended for 3 months and longer. The content of such particles in the suspension ranges from 3 to 12% depending on the WSCD concentration [5].

Quick formation of a transparent aqueous layer and flocculated sediment of charcoal particles was observed for suspensions containing starch, PVA, PAA, and PAAc. For the remaining suspensions, the sediments consisting of the largest particles were accumulated at the tube bottom only during the first two days. The volumes of the sediments in suspensions with Na-CMC and OPMC were approximately equal to those in the initial charcoal suspension; they were smaller for suspensions with WSCD and PVP and larger for suspensions with starch, PAAc, PVA, and PAA (Table 1). Moreover, it turned out that the particle concentration in the upper part of the suspension column was very low and comparable to the measurement error in all the suspensions except for those stabilized by PVP and WSCD.

The comparison of the volumes of sediments with the concentration of the dispersed phase in the bottom part of the suspension column indicates that the most loose sediments with free packing of particles are formed in the presence of PAA, PAAc, PVA, and starch, respectively. Sediment that is more compact compared to the initial charcoal was formed in the suspension modified by Na-CMC: at equal volumes of the sediments, the dispersed phase concentration is 1.5 times higher in the latter case. The experimental data correlate with the pattern of the particle size distribution: a broader distribution is observed for a looser sediment (Fig. 3e, 3f).

The experimental results indicate clearly that adsorption of polymers on the surface of charcoal particles differently affect the suspension stability. This fact can be interpreted as follows. On the one hand, bridging flocculation and, consequently, loss of aggregation stability followed by loss of sedimentation stability can occur upon adsorption. This phenomenon, in particular, is characteristic of suspensions modified by PAA, PVA, PAAc, and starch. On the other hand, steric

Table 1. Volume of sediment V and concentrations of dispersed-phase particles in the upper (φ_u) and lower (φ_l) parts of the column of 5% charcoal suspensions modified by polymers at 25°C

Polymer	V, cm^3	φ_u, wt %	φ_l, wt %
WSCD	2.5	0.48	9.08
PVP	3.0	0.28	19.06
OPMC	3.8	0.07	18.53
Na-CMC	4.1	0.06	21.57
Starch	8.3	0.03	13.95
PAAc	9.1	0.02	13.2
PVA	9.4	0.03	15.37
PAA	9.8	0.02	10.61
–	4	0.03	14.38

stabilization due to adsorption layers formed at the surface of charcoal particles by macromolecules of polymers, such as PVP and cellulose derivatives, can take place. These polymers are also likely to be responsible for peptization of particle aggregates. This is suggested by the fact that these polymers provide a narrower particle size distribution compared to the initial charcoal, with simultaneous decrease in the volume of sediments (Figs. 3b, 3c; Table 1). PVP falls out of this series to some extent (Fig. 3d): although it provides domination of the highly dispersed fraction of particles (5–10 μm) in the suspension, but simultaneously it forms a significant number of larger aggregates.

The highest stability is shown by suspensions containing PVP and WSCD. Probably it is related to enhanced affinity of these polymers to water (high hydrophilicity). For example, the rate of their dissolution with formation of 1% solutions exceeds the dissolution rate of the rest of the studied polymers by a factor of 100 and more, all other conditions being equal. The adsorption of PVP and WSCD on the surface of charcoal particles results in its marked hydrophilization, and hence the affinity of the interfacial layer to the dispersion medium increases to the highest extent.

Since the stability of disperse systems influences many of their properties and, in particular, determines the rheological behavior of suspensions, we studied modified charcoal suspensions under shear deformation. As was shown, FAC suspensions without polymer additives demonstrate virtually Newtonian flow in the range of the dispersed phase concentrations of 5–20% (Fig. 4a). Up from 21%, the flow curves comprise two portions: the portion of a sharp drop in the viscosity, indicative of the breakup of the suspension structure, and the portion of constant viscosity, characteristic of the flow of suspensions with a completely broken structure [6]. Along with the structure breakup, an additional factor reducing the suspension viscosity at an increasing shear stress can be orientation of anisometric charcoal particles in the flow. Structure formation in the suspension should be interpreted as establishment of coagulation contacts between particles and their aggregates. Also, since the experimental points coincide during deformation of disperse systems according to the scheme of “increasing–decreasing” shear stress, the structure can be described as thixotropic.

A similar behavior was characteristic of suspensions stabilized by PAA, PAAc, starch (Fig. 4b), as well as by Na-CMC and OPMC (Fig. 4c), with the only difference that the former polymers reduce and the latter ones raise the concentration of the dispersed phase corresponding to the transition of the charcoal suspension to non-Newtonian flow (Table 2). This concentration is virtually equal to the critical concentration of structure formation. Thus, beginning from some concentration, we observed behavior corresponding to weakly structured disperse systems, which are characterized by the presence of a region of flow with a completely broken structure.

At the same time, the portion with a sharp drop in the viscosity is absent on the rheograms of suspensions containing WSCD and PVP over the whole studied concentration range where suspensions still flow under the action of their own weight (Figs. 4e, 4f); i.e., these systems under dynamic conditions behave as virtually Newtonian liquids in a wide range of the dispersed phase concentrations. It should be noted that Newtonian flow is usually realized for aggregatively stable systems [7]. It is quite possible that Newtonian flow at low concentrations of the dispersed phase is due to the absence of structurization, and, at high concentrations, it is significant dispersity and surface hydrophilicity that determine strong fixation of anisometric charcoal particles in a continuous three-dimensional network, which does not fail in the studied range of shear stresses. At concentrations of the dispersed-phase particles exceeding 30%, the suspensions with WSCD and PVP demonstrate a slight increase in viscosity with increasing shear stress, which is characteristic of dila-

Table 2. Critical concentration of dispersed-phase particles φ_{cr} determined as the point of the transition to non-Newtonian flow for aqueous charcoal suspensions modified by different polymers

Polymer	PAA	PAAc	Starch	PVA	–	Na-CMC	OPMC	PVP	WSCD
φ_{cr}, wt %	6	9	11	12	21	21	28	–	–

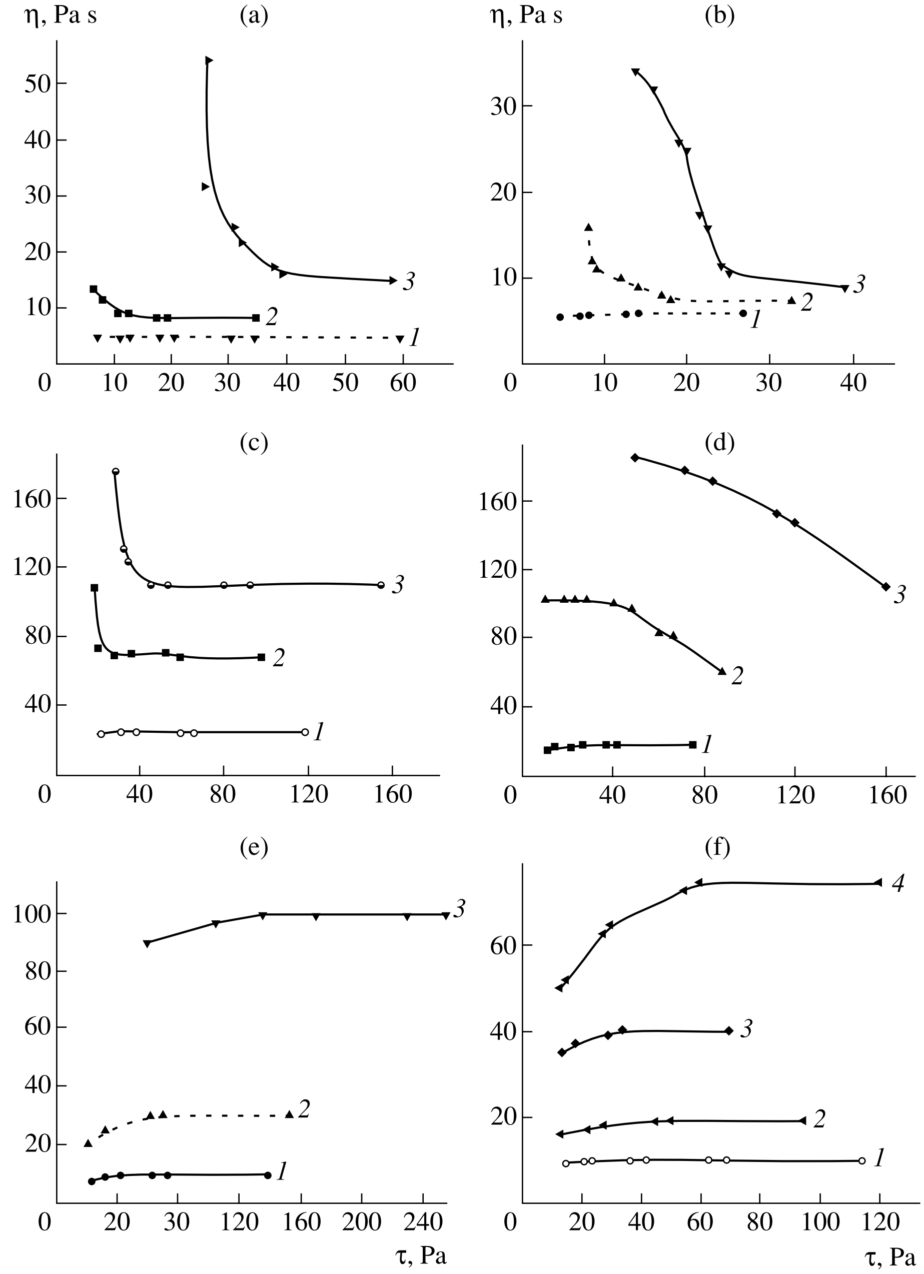

Fig. 4. Flow curves for suspensions of (a) the initial FDACF with dispersed phase concentrations (*1*) 17, (*2*) 21, and (*3*) 25% and for FDACF modified by (b) starch with dispersed phase concentrations (*1*) 10, (*2*) 12, and (*3*) 15%; (c) OPMC with dispersed phase concentrations (*1*) 25, (*2*) 28, and (*3*) 30%; (d) PVA with dispersed phase concentrations (*1*) 5, (*2*) 13, and (*3*) 18%; (e) PVP with dispersed phase concentrations (*1*) 25, (*2*) 30, and (*3*) 33%; and (f) WSCD with dispersed phase concentrations (*1*) 17, (*2*) 25, (*3*) 30, and (*4*) 35%.

tant systems; in the case of WSCD, this tendency is more pronounced. The possible cause of such behavior is the realization of flow in "confined" conditions at a high concentration of the dispersed phase under low loadings [8, p. 295].

A specific rheological behavior was also found for the suspension of charcoal modified by PVA (Fig. 4d). In this case, after the critical concentration is reached, a linear portion appears in the flow curves; it is indicative of reversible restoration of the structure in the process of its breakup, and the region of flow corresponding to the completely broken structure is absent. Further increase in the concentration of the dispersed phase is accompanied by an increase in the yield point determined by the Casson equation, and the linear portion of the curve disappears. For example, as the concentration changes from 13 to 18%, the yield stress increases from 4.3 to 5.0 Pa. It is this disperse system that shows the maximum viscosity.

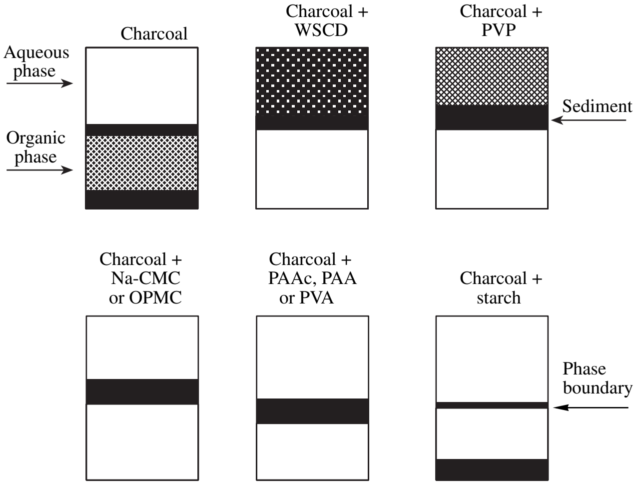

Fig. 5. Scheme of distribution between water and dichloromethane for particles of the FDACF, both original and modified by different polymers.

Thus, the rheological properties of suspensions correlate with the parameters of sedimentation stability. In particular, the concentration of the dispersed phase corresponding to the transition from Newtonian to non-Newtonian flow of suspensions can be recommended as a criterion of their stability.

As was mentioned above, the specific action of PVP and WSCD as polymeric stabilizers is due to their higher affinity to the dispersion medium compared to the rest of the above polymers and consequently to higher hydrophilization of the charcoal particle surfaces. This hydrophilization is confirmed not only by the high rate of dispersion in water but also by the distribution of the suspended particles between the aqueous and organic phases. As follows from Fig. 5, a stable suspension of charcoal in the water phase is formed only in the presence of PVP and WSCD. Some difference in the effects of these polymers is manifested in a larger volume of a sediment formed at the interface in the presence of PVP. The higher concentration of particles in the sediment (Table 1) and the broader particle size distribution (Fig. 3d) are also indicative of the lower stability of the suspension with PVP. The difference in the behavior of WSCD and PVP is most likely to be due to the polyelectrolyte nature of the former polymer; thus, steric stabilization is accompanied by electrostatic one. The charcoal particles of suspensions modified by other studied polymers are localized in the organic phase (starch) or near the interface in both aqueous (Na-CMC, OPMC) and organic phases (PAAc, PAA, PVA) in the form of a separate layer of a certain thickness.

Table 3. Time of disintegration in water t for charcoal tablets containing different polymeric binders

Binder	t, s
PAA	Over 3600
PAAc	210
PVA	180
Starch	150
OPMC	120
Na-CMC	30
PVP	25
WSCD	10

The high hydrophilization of charcoal in the presence of PVP and WSCD is confirmed by the data on the time of disintegration of charcoal tablets in water (Table 3). Thus, the tablets formed with PVP and WSCD undergo full disintegration in 25 and 10 s, respectively, with the formation of stable suspensions, whereas tablets containing PVA demonstrate only partial decomposition and tablets with PAA remain intact for 1 h.

CONCLUSIONS

1. The results of sedimentation analysis showed that the nature of polymers used for FAC modification affects the aggregation stability of charcoal suspensions. In the presence of PAA, PAAc, PVA, and starch, the suspensions are unstable with respect to aggregation and demonstrate fast sedimentation with the formation of loose sediments. On the contrary, Na-CMC, OPMC, WSCD, and PVP hinder the coagulation, enhance the stability of the suspensions and, as a rule, provide a narrower particle size distribution compared to that of the initial charcoal and the presence of a significant number of particles characterized by colloidal dispersity.

2. The patterns of the flow curves suggest that, depending on the presence and type of the polymeric binder, the studied charcoal suspensions at concentrations above the critical one mostly behave as structured disperse systems, their structure strength increasing with the concentration of the dispersed-phase particles.

3. Newtonian flow, which is characteristic of aggregatively stable systems, was demonstrated by suspensions modified with PVP and WSCD in a wide concentration range. In these suspensions, at significantly high concentrations of dispersed-phase particles, a three-dimensional network with strong fixation of anisometric hydrophilic highly dispersed charcoal particles can be formed without loss of sedimentation stability. The stabilizing effect of PVP and WSCD is due to their higher affinity to water compared to other polymers and hence to higher hydrophilization of the charcoal particle surfaces. In the case of WSCD, along with the structural–mechanical factor, the electrostatic factor of aggregation stability can also play a specific role.

4. A correlation between the stability and the rheological characteristics of aqueous charcoal suspensions was established. The concentration of the transition from Newtonian to non-Newtonian flow is proposed as a criterion of the stabilizing effect of polymers. The polymers providing a higher transition concentration compared to the initial charcoal suspension should be regarded as suspension stabilizers (Na-CMC, OPMC, PVP, and WSCD), and the polymers leading to a lower transition concentration—flocculants (PAA, PAAc, PVA, and starch).

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