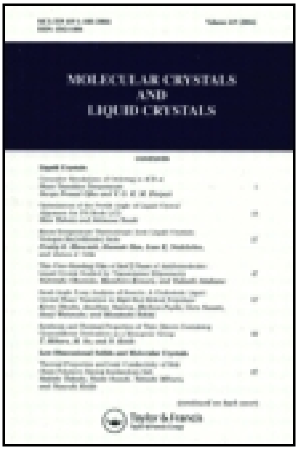

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Polyacrylamide-Grafted Silica for Environmental Protection

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Polyacrylamide-Grafted Silica for Environmental Protection

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The effect of grafts length on flocculation effectiveness of PAA-grafted silica for kaolin suspension ($R = 6.5\ \mu m$, $C = 30\,kg \cdot m^{-3}$) comparing with PAA and commercial flocculant Magnafloc LT-27 have been studied. It has been ascertained that nanocomposite with longer grafts is markedly better flocculant. The results of treatments of PAA-grafted silica which have been performed on the waterworks together with different nonionic (A227), anionic (A1020, A1050) and cationic (DB45SSH, KP555) commercial flocculants known in Ukraine are considered. It is shown that PAA-grafted silica alone removes up to 37% and in pair with coagulant up to 75% of pesticide during water clearing.

Keywords: flocculant; kaolin suspension; nanocomposite; polyacrylamide-grafted silica; tebuconazol

INTRODUCTION

Polymers at interfaces are of large importance in numerous applications. The properties of polymeric nanocomposites consisting of inorganic nanoparticles and organic polymers are strongly influenced by the nature of the filler/matrix interface. There are two ways to modify the surface of inorganic particles. The first one is carried out through surface absorption or reaction with small molecules. The second method is based on grafting polymeric molecules through covalent bonding to the hydroxyl groups existing on the particles. The advantage of the second procedure over the first one lies in the fact that the polymer-grafted particles can be provided with desired properties

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through a proper selection of the species of the grafting monomer and the grafting conditions. In this way, the structure-property relationship of the nanocomposites can be tailored on purpose. Thus the combination of silica surface adsorption capability and binding properties of polyacrylamide (PAA) chains in PAA-grafted particle allows developing perspective materials which could found application in wide range of industrial and environmental processes.

Nowadays, the environmental problems connected with purifying of natural water from pollutants, in particular, from pesticides, required new effective reagents and technologies. In such an ecological situation PAA-grafted silica flocculants [1] would be prospective examples combining high quality of drinking water according to international standards [2] and capability of pesticides removing at the stage of coagulative-flocculative process of water clearing at waterworks.

This report arises from our interest in functional capabilities of PAA-grafted silica as flocculant and depolluting reagent. Recently we have reported the synthesis and structural analysis of PAA-grafted silica [3,4]. In the present work we consider the effect of grafts molecular weight on flocculation efficiency of PAA-grafted silica for kaolin suspension ($R = 6.5\,\mu m$, $C = 30\,kg \cdot m^{-3}$) comparing with PAA and commercial flocculant Magnafloc LT-27. The treatment of PAA-grafted silica has been performed on the waterworks during water purifying together with different nonionic (A227), anionic (A1020, A1050) and cationic (DB45SSH, KP555) commercial flocculants known in Ukraine. Here the results of pesticide removing by PAA-grafted silica during clearing water polluted with tebuconazol are presented.

EXPERIMENTAL

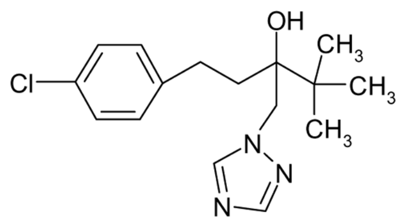
PAA-grafted silica nanocomposites have been synthesized using cerium-ion-initiated solution polymerization technique at room temperature in aqueous medium [5]. The following materials have been used for the synthesis of the polymer-grafted particle: (i) monomer acrylamide, Reanal, Hungary; (ii) ammonium cerium (IV) nitrate, Aldrich, USA. Silica nanoparticles used was Aerosil A-175, Orisil, Ukraine with BET surface area $185\,m^2/g$. The average grafts number N was calculated to be on average 23 grafts per 1 silica particle from elementary analysis data. The confirmation of silica availability in grafted product was carried out by elemental analysis [3]. The samples with different grafts molecular weight have been obtained by variation of monomer and initiator concentration ratio. Main characteristics of PAA-grafted silica are presented in Table 1. Homopolymer with $Mv = 1.25 \cdot 10^6$ which was used for comparing in flocculation tests

TABLE 1 Main Characteristics of PAA-Grafted Silica

Sample	R_{SiO2} (nm)	$M_{vPAA} \cdot 10^{-6}$	N_{PAA}[a]
PAA-grafted1 silica	7.7	1.6	23
PAA-grafted2 silica	7.7	3.8	23

[a]The grafts number per 1 silica particle.

have been obtained using the same experimental procedure, initiated by redox system consisting of ceric ions and water molecules. Commercial flocculant – weak-anionic Magnafloc LT-27, Allied Colloids, UK was studied for comparative evaluation in flocculation tests. Also tebuconazol – the system fungicide of broad action spectrum, Bayer, Germany (chromatography standard) have been applied:



The flocculation studies on model kaolin suspension with the predominant particle size $R = 6.5\mu m$ and $C = 30\,kg \cdot m^{-3}$ were carried out using settling tests at 293 K. The natural kaolin from Glukhovetskoye deposit, Ukraine, which exact chemical composition is well known [6] was used. The settling tests following the flocculation of the particles were carried out in 50 ml graduated cylinder by recording the height of clarified pillar as a function of time. The content of the cylinder was inverted 10 times during 15 seconds before being allowed to settle for observation of flocculation and sedimentation. The optical density (turbidity) of supernatants was measured with spectrophotometer SF-46 LOMO, Russia at $\lambda = 540\,nm$ (far from the polymer absorption bands) in 20 minutes after the specified period of inverting.

The clearing process of water using PAA-grafted silica together with different nonionic (A227), anionic (A1020, A1050) and cationic (DB45SSH, KP1020) commercial flocculants known in Ukraine has been performed at the waterworks. The purifying ability of flocculants was characterized by a method of "test coagulation" [2], which imitate the technological process. In a beaker containing $2\,dm^3$ of river water the coagulant (aluminum sulfate), chlorine water and flocculant were added successively. The dispersion was stirred for 1 minute at 140 rpm and then for 11 minutes at 45 rpm. Stirring was stopped and water was allowed to settle down for 30 minutes. Cleared water was carefully taken with siphon from 5 cm height below liquid level for the analysis. Three criteria of water quality were determined subsequently following international standards [2]: turbidity, chromaticity and content of residual aluminum. The chromaticity was determined by spectrophotometry at $\lambda = 413$ nm according to the Ukrainian State Standard 3351-74. Water probes, which have been filtrated through membrane filter with pores diameter $D = 0.45\,\mu$m, were compared with calibration solutions of different concentration simulating the color of natural water [2]. $K_2Cr_2O_7$, $CoSO_4$, sulphuric acid and distilled water were used for the preparing of calibration solutions. The chromaticity of water was characterized by °Cr−Co scale in the same concentration units as calibration solutions ($mg \cdot dm^{-3}$). The turbidity was also determined by spectrophotometry at $\lambda = 540$ nm according to the same Ukrainian State Standard 3351-74. Water probes were compared with standard kaolin suspensions, obtained by dilution of the main suspension with kaolin concentration $\sim 4\,g \cdot dm^{-3}$.

The modeling of a coagulative-flocculative process of water clearing in the presence of pesticide tebuconazol (introduced doze $0.1\,mg \cdot dm^{-3}$ at limit permissible concentration $0.025\,mg \cdot dm^{-3}$) was carried out in the laboratory using natural water (Desna river), above mentioned “test coagulation” method, the same purifying reagents as in real process and flocculant PAA-grafted2 silica. The quantitative analysis of tebuconazol was carried out by gas-liquid chromatography on “Net-Chrom” chromatograph (Russia) with computer processing of detector signals. The samples for tebuconazol determination have been prepared as described in Ref. [7].

RESULTS AND DISCUSSION

The typical results of settling tests when studding kaolin suspension and flocculant are presented in Figures 1 and 2 for PAA-grafted1 silica and PAA-grafted2 silica respectively. The flocculation capability of Unicomfloc samples was characterized through the following parameters: (i) duration of initial stage of primary aggregation of the colloid particles (τ_0); (ii) the relative (in comparison with the rate of suspension sedimentation in water) velocity of the rapid stage of flocculation (υ_{rel}); (iii) the volume of precipitate per settling time of 1 minute (V). These parameters were assigned from the precipitation curves. The significance of υ_{rel} determination is clear. We suggest

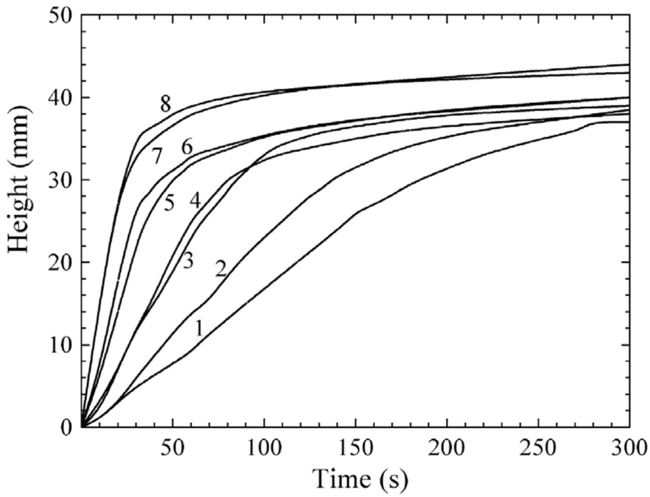


FIGURE 1 Variation of the height of purified kaolin suspension pillar with time in water – curve 1 and at PAA-grafted1 silica doses of $1 \cdot 10^{-4}$ – curve 2, $5 \cdot 10^{-4}$ – curve 3, $1 \cdot 10^{-3}$ – curve 4, $5 \cdot 10^{-3}$ – curve 5, $1 \cdot 10^{-2}$ – curve 6, $5 \cdot 10^{-2}$ – curve 7, $1 \cdot 10^{-1}$ – curve 8 ($kg \cdot m^{-3}$).

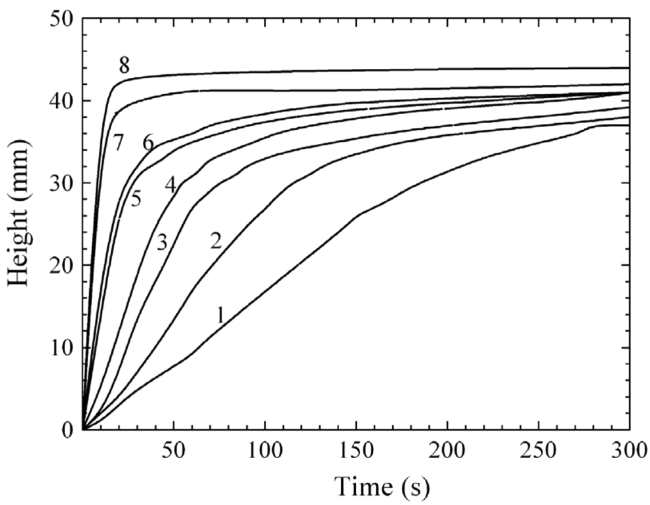


FIGURE 2 Variation of the height of purified kaolin suspension pillar with time in water – curve 1 and at PAA-grafted2 silica doses of $1 \cdot 10^{-4}$ – curve 2, $5 \cdot 10^{-4}$ – curve 3, $1 \cdot 10^{-3}$ – curve 4, $5 \cdot 10^{-3}$ – curve 5, $1 \cdot 10^{-2}$ – curve 6, $5 \cdot 10^{-2}$ – curve 7, $1 \cdot 10^{-1}$ – curve 8 ($kg \cdot m^{-3}$).

two more parameters, which are very important for estimation of flocculative capability. Really, τ_0 characterizes the duration of flocculant macromolecules interaction with the particles of dispersed phase (adsorption on the large particles and complex formation with the small ones) and primary aggregation of the colloid particles. In fact, the formation of primary flocs, which then swiftly settle, occurs on this process stage. Two different flocculants can be characterized by the same υ_{rel} values but different τ_0 values. In this case the higher velocity of the whole process would be realized for the flocculant with the lesser τ_0 value. The precipitate volume that is formed for certain time period (in our experiments it was 1 minute) is directly connected with the primary floc compactness [8]. The results of flocculation studies by laser diagnostics [9] have showed that the greatest flocs compactness occurs in a concentration region, where polymers reveal the highest flocculative efficiency producing the minimum precipitate. One more parameter, which characterized the clarifying degree of suspension, the optical density (D) of supernatants was measured in 20 minutes after the precipitation started. The large majority of suspension particles settle per 10 minutes. We have chosen 20 minutes in order to characterize the degree of removal of smallest particles of kaolin suspension during flocculation. The most of parameters, presented in Table 2, show that flocculation efficiency of nanocomposite with longer grafts is markedly better than that of the sample with fewer grafts molecular weight, PAA and Magnafloc LT-27 used for kaolin suspension, in such way as high settling rate, dense floccules, low values of initial stage time of colloid particles primary aggregation and optical density of supernatants.

The sample with better flocculation results namely PAA-grafted2 silica was applied in water purification tests. The example of the purifying effect of coagulant only and of coagulant pairs with different flocculants of water from Desna River are brought together in Table 3. The tests of PAA-grafted2 silica flocculation capability showed that they work at the level of flocculants, known in Ukraine. The treatments have been carried out in autumn on the water with high turbidity and chromaticity indexes. By some indexes PAA-grafted2 silica demonstrates higher efficiency.

Experiments with removing of pesticide from natural water during the model coagulative-flocculative clearing process constitute the most interesting and important part of this work. They allowed determining the degree of removal of pesticide – tebuconazol at extremely small introduced concentration 0.1 $mg \cdot dm^{-3}$, though high as for potable water (limited permissible concentration is 0.025 $mg \cdot dm^{-3}$) in the presence of various “background” substances, which usually occur in

TABLE 2 Results of Kaolin Suspension ($30\,kg \cdot m^{-3}$) Settling by Different Flocculants

Flocculant	$C \cdot 10^3$ ($kg \cdot m^{-3}$)	υ_{rel}	τ_0 (s)	V (cm^3)	D
PAA-grafted1 silica	0.01	1.3	15	34	0.155
	0.05	2	4	27	0.175
	0.1	2.5	2	25	0.131
	0.5	4.3	1	18	0.055
	1	5.5	0	17	0.035
	5	6.47	0	12	0.023
	10	8.2	0	11	0.02
PAA-grafted2 silica	0.01	1.2	14	35	0.175
	0.05	2.6	4	23	0.136
	0.1	3.4	1	20	0.125
	0.5	7	0	15	0.043
	1	8.8	0	12	0.025
	5	26.5	0	9	0.023
	10	26.8	0	8	0.03
PAA	0.01	1.24	15	34	0.142
	0.05	1.8	6	30	0.165
	0.1	2.16	4	25	0.19
	0.5	3.6	1	21	0.07
	1	5.29	0	17	0.055
	5	7	0	15	0.027
	10	7.8	0	12	0.02
Magnaflok LT-27 (Allied Colloids)	0.1	1.69	15	34	0.473
	0.5	1.56	16	37	0.422
	1	3.06	11	23	0.553
	5	11.19	0	12.25	0.302
	10	20	0	10	0.164

natural waters and competitively interact with coagulants and flocculants. Figure 3 shows the picture of chlorine river water polluted with tebuconazol. The quantity of introduced pesticide was found to be $0.0811\,mg \cdot dm^{-3}$ (Table 4), which is in the level of metrological characteristics of this determination method. Flocculant alone and coagulant alone somewhat decrease this concentration to $0.051\,mg \cdot dm^{-3}$ and $0.0549\,mg \cdot dm^{-3}$ accordingly (Figures are not presented. See Table 4). Flocculant in pair with coagulant decreases introduced dose of tebuconazol in 4 times. The pesticide concentration after water purification becomes not higher that limited permissible concentration (Fig. 4, Table 4). So PAA-grafted2 silica interacts with tebuconazol during water purification. One can suppose the following types of interaction: 1 – electrostatic coupling of positively charged of triazole ring of tebuconazol with negative charged surface of silica; 2 – the interaction of

TABLE 3 Parameters of Natural Water after Purifying with Different Flocculants

Flocculant	Dose ($mg \cdot dm^{-3}$)[a] $Al_2(SO_4)_3 \cdot 18H_2O$	Dose ($mg \cdot dm^{-3}$)[a] Flocculant	Turbidity ($mg \cdot dm^{-3}$)	Chromaticity (°Cr–Co scale)	Residual Al ($mg \cdot dm^{-3}$)
–	10	–	3.7	17	0.8
–	20	–	2.4	14	0.9
–	30	–	2.0	13	1.05
PAA-grafted	30	0.1	1.6	13	0.8
silica	30	0.3	1.2	13	0.76
A1020	30	0.1	1.9	12	0.87
	30	0.3	1.7	12	0.8
A227	30	0.1	1.5	13	0.87
	30	0.3	1.1	12	0.8
KP555	30	0.1	2.2	13	0.8
	30	0.3	1.0	12	0.77
A1050	30	0.1	2.3	12	0.99
	30	0.3	1.9	12	0.92
DB45SSH	30	0.1	2.2	14	0.8
	30	0.3	1.9	11	0.76

[a]Doses of NH_3 and of chlorine water were 0.3 and 2.5 $mg \cdot dm^{-3}$ respectively.

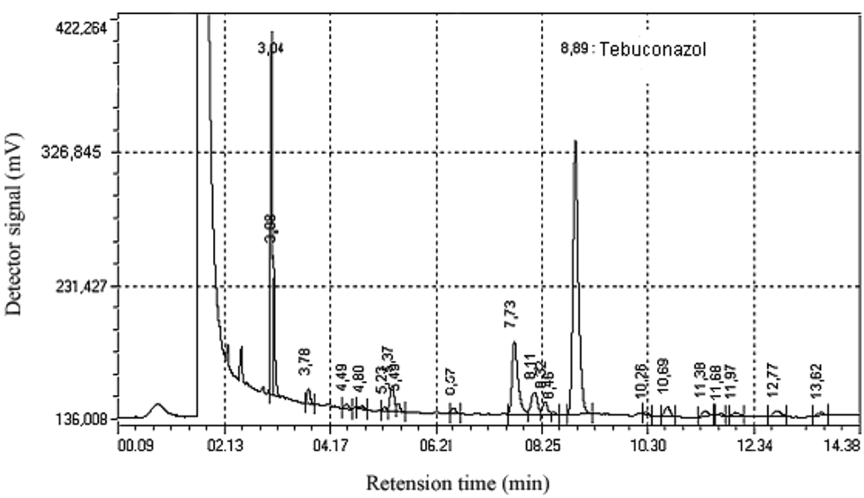


FIGURE 3 Chromatogram of chlorine and polluted with tebuconazol river water.

TABLE 4 The Results of Tebuconazol Determination in Nature Water after Purification

Purifying reagent	$C_{\text{tebuconazol}}$ (mg · dm^{-3})
–	0.0811
Flocculant + coagulant	0.0205
Coagulant	0.0549
Flocculant	0.0511

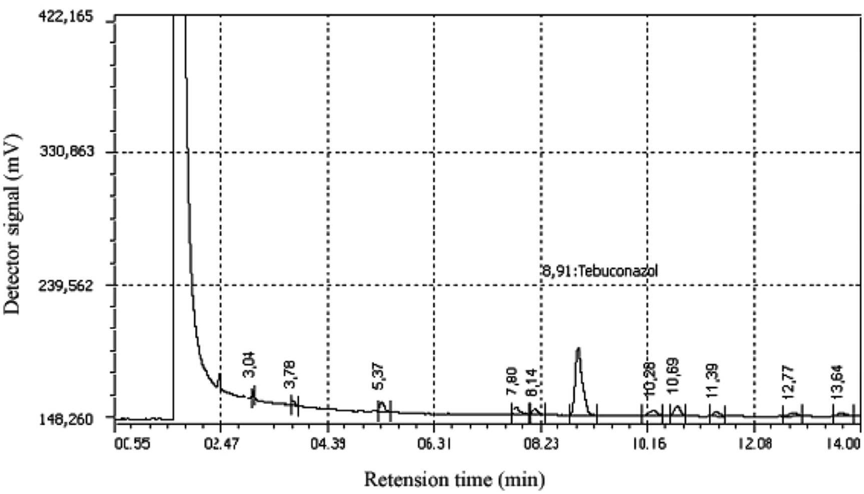


FIGURE 4 Chromatogram of chlorine and polluted with tebuconazol river water after treating with flocculant PAA-grafted2 silica and coagulant.

polyacrylamide amide groups with hydroxyl tebuconazol groups through hydrogen bonds; 3 – binding of benzene ring of tebuconazol with silica silanol groups through hydrogen bonds.

CONCLUSIONS

It has been ascertained that flocculation capability of PAA-grafted silica with longer grafts is markedly better than that of the sample with fewer grafts molecular weight, PAA and Magnafloc LT-27 used for kaolin suspension, in such way as high settling rate, dense floccules, low values of initial stage time of colloid particles primary aggregation and optical density of supernatants. The investigation results during treatments by "test coagulation" method on waterworks have demonstrated not worse but sometimes the better standard quality parameters of cleared water with using of PAA-grafted silica than that with commercial flocculants. It was shown that PAA-grafted silica nanocomposites can bee particularly attractive at solving the environmental protection problem such as water pollution with pesticides. At introduced dose of tebuconazol $0.1\,\mathrm{mg}\cdot\mathrm{dm}^{-3}$ into the river water PAA-grafted silica alone removes up to 37% and in pair with coagulant up to 75% of pesticide during water clearing which copies the technological process.

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