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Use of Chitosan for Textile Wastewater Decolourization

DOI: 10.5604/12303666.1196623

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Abstract
The aim of the study was to investigate the effectiveness of decolourization of various types of textile wastewater by coagulation with the use of chitosan while ensuring high process efficiency. The effects of decolourization depended on the composition and ionic nature of compounds present in the wastewater. Additional use of ferrous sulfate next to chitosan in the coagulation processes increased the level of wastewater decolourization to about 99%.

Key words: *textile wastewater, chitosan, decolourization.*

Introduction

Colour is one of the basic indices which describe the quality of water used for both municipal and industrial purposes. Thus decolourization problems are equally important for wastewater treatment technology and water conditioning. Coagulation can significantly reduce the concentration of pollutants in wastewater. A 70 - 80% decolourisation and similar reduction in the concentration of organic compounds can be achieved. This is one of the simplest and cheapest methods readily applicable in industrial plants. The methods of coagulation are in the focus of attention, which is evidenced by a large number of papers on this subject published in scientific journals [1 - 4].

Two basic types of coagulants, i.e. inorganic and organic, are used in the processes of coagulation [5 - 7]. The first ones contain primarily aluminum and iron salts. The use of inorganic coagulants is not particularly preferred because after purification metal ions from coagulants may occur in the wastewater treated. It is preferable to use organic compounds – polyelectrolytes, especially those of cationic nature. This is due to the prevalence of anionic compounds in textile wastewater, which increases the effectiveness of treatment.

Organic coagulants based on synthetic polymers have many advantages over inorganic coagulants. These include smaller doses required in the process of coagulation and lower sensitivity to pH values. However, coagulants which are synthetic polymers also have some disadvantages, for example they are quite expensive, not biodegradable, and are often characterised by significant toxicity [5], which is why high interest in natural polymers as an alternative to synthetic polyelectrolytes is observed presently. They are called bioflocculants and contain biopolymers such as starch, chitosan and algae. Bioflocculants are safe for aquatic organisms, are easily biodegradable, and do not create secondary pollutants. It can be expected that the consumption of biocoagulants and bioflocculants will grow and be increasingly used in wastewater treatment technologies and water conditioning. An especially promising bioflocculant is chitosan.

Chitosan is an aminopolysaccharide obtained in the process of deacetylation of chitin, which, besides cellulose, is the most common natural polymer in the world [8]. Its main source are organisms living in sea water – shrimps and crabs. Chitosan has unique properties as compared to other biopolymers which result from the presence of primary amino groups. Its main advantages are non-toxicity and biodegradability. It is obtained from natural and renewable environmentally friendly sources.

Chitosan is used, inter alia, in wastewater treatment and water conditioning. It easily forms complex compounds with pollutants present in water. It is used as a flocculant and coagulant in the removal of pollutants contained in various types of industrial wastewater [9 - 11]. Recently reports on the possibility of using chitosan for treatment, especially for the removal of dyes from wastewater, have been published [12 - 17]. Chitosan is an efficient coagulant in wastewater treatment even at low temperatures and in much smaller doses than the doses of conventional coagulants required. When using chitosan as a coagulant, its dose required for treatment of a particular type of wastewater should be determined precisely. Exceeding of the optimum dose causes destabilisation of the sludge formed and worsens the effects of treatment. It is also possible to use chitosan in combination with other coagulants, both organic (polyelectrolytes) and inorganic (metal salts), which can increase the effectiveness of treatment processes.

Due to the fact that chitosan may have different efficiency in the treatment of particular types of textile wastewater with different compositions and concentrations of pollutants, it is important to determine its optimum dose depending on the nature and composition of the wastewater. Therefore the aim of this study was to examine the effectiveness of the decolourisation of particular types of textile wastewater by coagulation with the use of chitosan, ensuring high process efficiency at the same time.

Materials, method and equipment

Materials

The subject of research was model wastewater from cotton dyeing with reactive and direct dyes. It contained direct and reactive dyes (Direct Red 23 and Reactive Red 120), salt, acetic acid, soda ash and chemicals of anionic (Dekol SAD), cationic (Perrustol IPD) or nonionic (Rucofin GWA) nature. The pH of the wastewater was about 10,7. Tests on the model wastewater were subsequently verified based on real wastewater which came from a textile plant in Łódź where textiles from cellulose fibres were dyed. Differences between values of absorbance result from the fact that model wastewater was concentrated dyeing bath with intensive colour, while the real one was average industrial textile wastewater with less intensive colour.

The wastewater was purified using chitosan and a mixture of chitosan and ferrous sulfate as a coagulant. The initial biopolymer was ground, sieved, and then a fraction with a grain size smaller than 60 microns was collected. Next 1 g of chitosan was placed in a 100 ml flask, to which 98 ml of demineralised water was added. After 24 hours 1 g of 80% acetic acid solution was added to the flask. The solution was stirred and then left undisturbed for a further 24 hours [13]. The chitosan solution was used in the coagulation process. The hydrolysis of chitosan acetate was not observed. Ferrous sulfate in a solid state was added directly to the wastewater.

Methods and conditions of experiments

The coagulation process was carried out by adding a specified dose of coagulant to the wastewater. Next the wastewater was stirred vigorously for 2 minutes and then slowly for a further 5 minutes. After the precipitation of sludge the solution was allowed to stand for 2 hours. Then the solution was filtered through a filter paper and samples taken for analysis.

After the treatment, the colour of the wastewater samples was determined by the *DFZ* method. The spectral absorption coefficient (*DFZ*, *Durchsichtsfarbzahl* in German) was determined on the basis of absorbance measurements by the spectrophotometric method at three wavelengths (λ = 436, 525 and 620 nm), using the formula

$$DFZ = 1000\, E(\lambda)/d \text{ in l/m}$$

where, $E(\lambda)$ is the absorbance at a given wavelength λ, and d is the measuring cuvette thickness in mm.

Experimental equipment

Spectrophotometric analysis was made with the use of JASCO V-630 (JASCO, Japan) apparatus.

Results

Decolourisation of textile wastewater with the use of chitosan

Wastewater containing anionic chemicals

Figure 1 shows changes in the spectrum of wastewater containing anionic chemicals depending on the dose of chitosan.

As follows from the data, initially with an increase in the coagulant dose the level of wastewater decolourization increased. The best results were obtained at a dose of 50 mg chitosan/dm^3. A further increase in the coagulant dose resulted in a reduction in wastewater decolourisation. The results are consistent with those obtained by other authors who dealt with the decolourization of water solutions of pure dyes and who observed that exceeding the optimum dose of chitosan caused destabilization of the sludge formed and worsened the effects of the treatment [9]. As can be seen, a similar relationship is obtained in the case of wastewater decolourisation.

Table 1 summarises the results of colour determination in the wastewater (*DFZ*) and presents calculated levels of colour

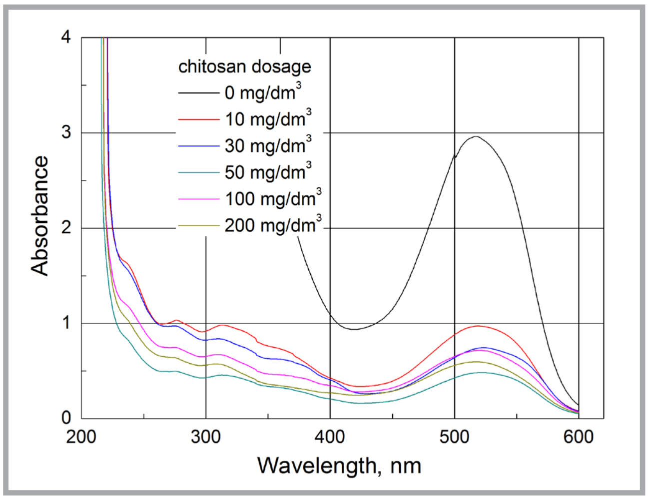

Figure 1. *Changes in the spectrum of textile wastewater containing anionic chemicals subjected to coagulation depending on the dose of chitosan.*

Table 1. *Results of colour determination (DFZ) in the wastewater depending on the chitosan dose and calculated levels of colour reduction after the coagulation process in relation to wastewater before treatment. Initial DFZ values at wavelength 436 nm – 99.5, 525 nm – 290.9, 620 nm – 14.*

Treatment parameters	Dose of chitosan, mg/dm^3				
	10	30	50	100	200
DFZ in 1/m at wavelength 436 nm 525 nm 620 nm	 34.9 96.5 8.0	 26.6 74.4 7.7	 16.7 48.3 5.2	 29.2 71.3 7.1	 25.9 58.8 6.1
DFZ reduction in % at wavelength 436 nm 525 nm 620 nm	 64.9 66.8 42.8	 73.3 74.4 45.1	 83.2 83.4 62.8	 70.7 75.5 49.3	 73.9 79.8 56.2

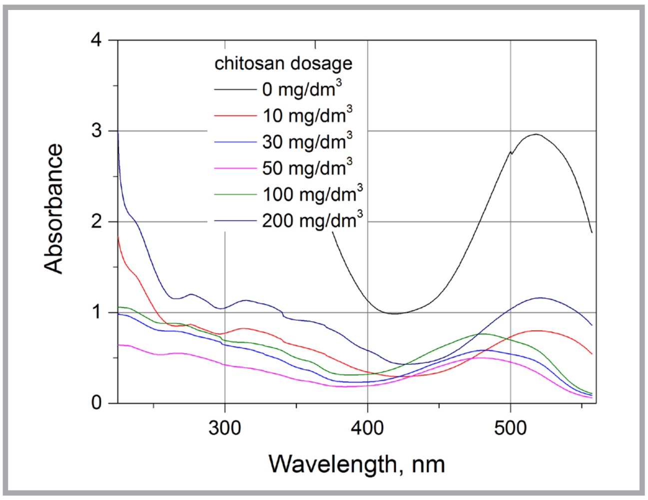

Figure 2. Changes in the spectrum of textile wastewater containing cationic chemicals subjected to coagulation dependent on the chitosan dose.

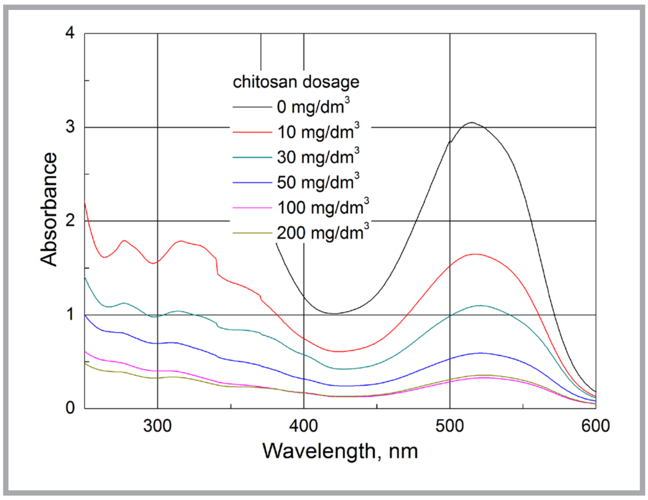

Figure 3. Changes in the spectrum of textile wastewater containing nonionic compounds subjected to coagulation depending on the chitosan dose.

reduction after the coagulation process in relation to the wastewater before treatment. The highest level of *DFZ* reduction was achieved at a chitosan dose of 50 mg/dm^3. At wavelengths of 436, 525 and 620 nm it was 83, 83 and 63%, respectively. Hence colour removal from the wastewater was good.

Wastewater containing cationic chemicals

Figure 2 shows changes in the spectrum of wastewater containing cationic chemicals dependent on the chitosan dose.

As follows from the data, initially with an increase in the coagulant dose the level of wastewater decolourization increased. The best results were obtained at a chitosan dose of 30 mg/dm^3. The dose was nearly half the size of the optimal in the case of wastewater containing anionic compounds. The wastewater containing cationic compounds was therefore more sensitive to the chitosan dose. To obtain a maximum decolourization, a much smaller dose of the coagulant was required. Increasing the dose of chitosan above the optimal one resulted in a significant decrease in decolourisation efficiency.

Table 2 summarises results of colour determination in the wastewater (*DFZ*) and presents calculated levels of colour reduction after the coagulation process in relation to the wastewater prior to treatment.

The highest *DFZ* reduction was obtained at a chitosan dose of 50 mg/dm^3. At wavelengths 436, 525 and 620 nm it was 78, 80 and 51%, respectively. Thus the decolourisation of wastewater containing cationic compounds was as good as that of the wastewater comprising anionic chemicals.

Wastewater containing nonionic compounds

Figure 3 shows changes in the spectrum of wastewater containing nonionic compounds depending on the chitosan dose.

As is seen from the data, with an increase in the coagulant dose the level of wastewater decolourisation grew. At a chitosan dose of 100 mg/dm^3 it was the highest. A further increase in the dose to 200 mg/dm^3 neither improved the level of decolourization nor worsened it. Thus the optimal dose was 100 mg/dm^3. Contrary to the wastewater containing anionic and cationic compounds, in the wastewater comprising nonionic chemicals in the range of chitosan doses tested, after reaching a certain limiting value, no worsening of the wastewater decolourisation with an increase in the dose was observed.

Table 2. Results of colour determination (DFZ) depending on the chitosan dose and calculated values of colour reduction after the coagulation process as compared to the wastewater before treatment. Initial DFZ at wavelength 436 nm – 104.3, 525 nm – 291.5, 620 nm – 17.0.

Treatment parameters	Dose of chitosan, mg/dm^3				
	10	30	50	100	200
DFZ in 1/m at wavelength					
436 nm	31.3	23.3	18.7	30.5	43.9
525 nm	76.4	58.5	50.0	79.3	115.7
620 nm	10.8	8.9	6.3	7.6	11.5
DFZ reduction in % at wavelength					
436 nm	69.8	77.5	82.0	70.6	57.7
525 nm	73.9	80.0	82.9	72.9	60.4
620 nm	39.9	50.7	65.2	57.7	36.1

Table 3. Results of colour determination (DFZ) depending on the chitosan dose and calculated values of colour reduction after the coagulation process as compared to the waste-water before treatment. The initial DFZ at wavelength 436 nm – 106.5, 525 nm – 297.8, 620 nm – 17.7.

Treatment parameters	Dose of chitosan, mg/dm^3				
	10	30	50	100	200
DFZ in 1/m at wavelength					
436 nm	62.9	43.0	24.4	12.7	13.3
525 nm	162.7	109.3	58.9	32.9	35.7
620 nm	13.0	1.5	8.2	5.1	5.4
DFZ reduction in % at wavelength					
436 nm	40.9	59.7	77.0	88.1	87.5
525 nm	45.4	63.3	80.2	88.9	88.0
620 nm	26.7	35.1	53.9	71.3	69.5

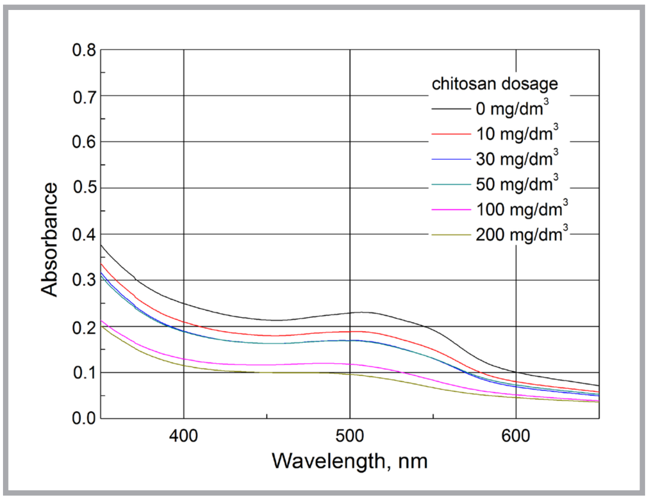

Figure 4. Changes in the spectrum of real wastewater subjected to coagulation as compared to the initial wastewater.

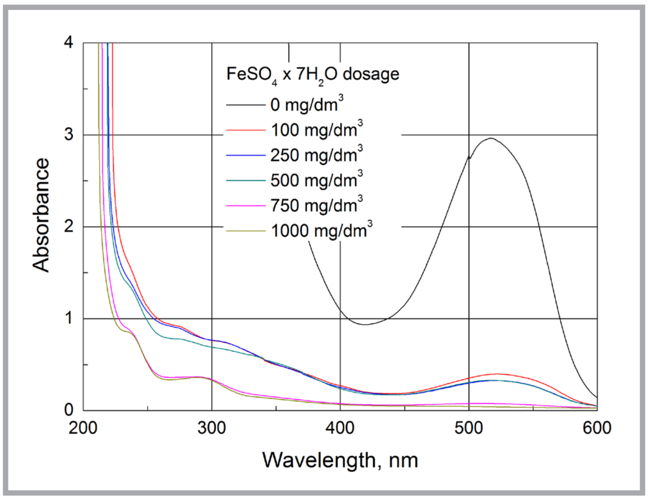

Figure 5. Changes in the spectrum of textile wastewater containing anionic compounds subjected to coagulation depending on the ferrous sulfate dose at a chitosan dose of 50 mg/dm3.

Table 3 summarises results of colour determination in the wastewater (*DFZ*) and presents calculated levels of colour reduction after the coagulation process in relation to the wastewater prior to treatment. The highest level of *DFZ* reduction was obtained at a dose of chitosan equal to 100 mg/dm^3. At wavelengths 436, 525 and 620 nm it was 88, 89 and 71%, respectively. Thus colour removal from the wastewater containing nonionic compounds was very good.

Comparing the results for the three types of model wastewater, it should be noted that the resulting maximum decolourisation of the samples as well as the optimal doses of chitosan varied considerably. It clearly depended on the composition of wastewater and its ionic character. The highest level of decolourisation was obtained after coagulation of the wastewater containing nonionic compounds. For instance, at wavelength 525 nm (close to the absorbance peak) colour reduction for the wastewater with nonionic, anionic and cationic compounds was 88.9%, 83.4% and 82.9%, respectively. The optimal doses of chitosan were 50 mg/dm^3 (wastewater with anionic compounds), 50 mg/dm^3 (wastewater with cationic compounds) and 100 mg/dm^3 (wastewater with nonionic chemicals).

Real wastewater

In the next stage of the research results obtained from the model wastewater were verified based on the real wastewater from one of the Łódź textile plants where products made from cellulose fibres were dyed. ***Figure 4*** shows changes in the spectrum of real wastewater depending on chitosan doses. As seen from these data, with an increase in the coagulant dose, wastewater decolourisation increased, reaching the highest level at the biggest chitosan dose, i.e. 200 mg/dm^3. The relationships were similar to those obtained for the model wastewater containing a nonionic compound. No worsening of the level of wastewater decolourisation was observed when increasing chitosan doses in the range tested.

Table 4 summarises results of colour determination in the wastewater (*DFZ*) and presents calculated levels of colour reduction after the coagulation process in relation to the wastewater before treatment.

The highest level of *DFZ* reduction was obtained at a chitosan dose of 200 mg/dm^3, which was 54, 62 and 53% at wavelengths 436, 525 and 620 nm, respectively. Hence decolourisation of the wastewater was quite good.

Decolourisation of textile wastewater with the use of chitosan and ferrous sulfate

The next step of the research was the decolourisation of wastewater with the con-

Table 4. *Results of colour determination (DFZ) depending on the chitosan dose and calculated values of colour reduction after the coagulation process as compared to the wastewater before treatment. Initial DFZ at wavelength 436 nm – 21.9, 525 nm – 22.1, 620 nm – 8.8.*

Treatment parameters	Dose of chitosan, mg/dm3				
	10	30	50	100	200
DFZ in 1/m at wavelength 436 nm 525 nm 620 nm	 18.3 17.8 7.0	 16.6 15.8 6.0	 16.6 15.7 6.4	 11.7 10.5 4.6	 10.2 8.4 4.1
DFZ reduction in % at wavelength 436 nm 525 nm 620 nm	 16.2 19.4 20.0	 24.3 28.4 31.5	 24.4 28.8 27.1	 46.6 52.4 47.8	 53.7 61.8 53.0

Table 5. *Results of colour determination (DFZ) depending on the ferrous sulfate dose at a chitosan dose of 50 mg/dm3 and calculated values of colour reduction after the coagulation process as compared to the wastewater before treatment. Initial DFZ at wavelength 436 nm – 99.5, 525 nm – 290.9, 620 nm – 14.*

Treatment parameters	Dose of ferrous sulfate, mg/dm3				
	100	250	500	750	1000
DFZ in 1/m at wavelength 436 nm 525 nm 620 nm	 18.6 39.7 5.5	 17.7 32.6 5.1	 17.2 32.7 5.2	 6.1 7.5 3.1	 5.2 4.0 2.9
DFZ reduction in % at wavelength 436 nm 525 nm 620 nm	 81.3 86.3 60.4	 82.2 88.8 63.5	 82.7 88.8 63.5	 93.8 97.4 77.6	 94.8 98.6 79.6

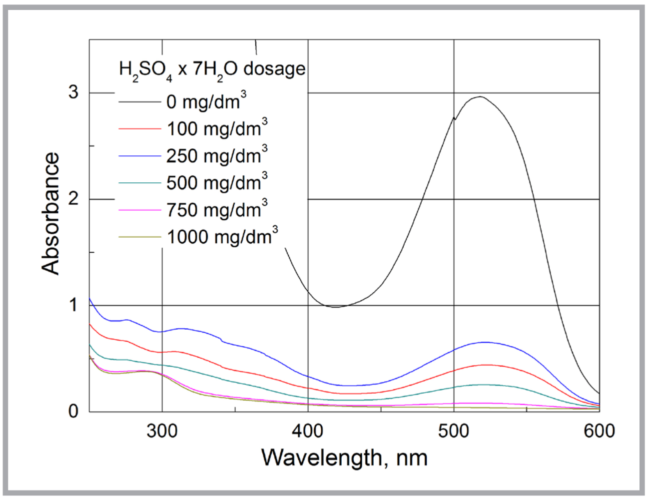

Figure 6. *Changes in the spectrum of textile wastewater containing cationic compounds subjected to coagulation in dependence on the ferrous sulfate dose at a chitosan dose of 30 mg/dm3.*

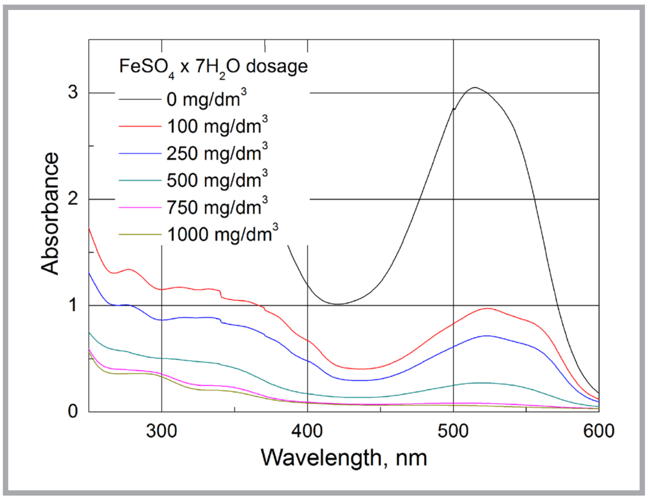

Figure 7. *Changes in the spectrum of textile wastewater containing nonionic compounds subjected to coagulation depending on the ferrous sulfate dose at chitosan dose of 100 mg/dm3.*

comitant use of chitosan and ferrous sulfate. The aim of the research was to study the possibility of enhancing the level of wastewater decolourisation by the application of an inorganic coagulant besides chitosan.

Wastewater containing anionic compounds

Figure 5 (see page 133) shows changes in the spectrum of wastewater containing anionic compounds depending on the dose of ferrous sulfate at a previously determined optimal chitosan dose of 50 mg/dm3 (cf. ***Figure 1***).

As follows from these data, initially with an increasing dose of ferrous sulfate the decolourisation of wastewater increased and was quite similar in the dose range of 100 to 500 mg/dm3. At higher doses of ferrous sulfate ranging from 750 to 1000 mg/dm3, the decolourization of wastewater was practically complete.

Table 5 (see page 133) summarises results of colour determination in the wastewater (DFZ) and presents calculated levels of colour reduction after the coagulation process in relation to the wastewater before treatment.

The highest *DFZ* reduction was obtained at a dose of ferrous sulfate equal to 1000 mg/dm3. At wavelengths 436, 525 and 620 nm it was 95, 99 and 80%, respectively. Thus the wastewater was almost completely decolourized. Results of the decolourization were much better (by 15 to 20%) than in the case where chitosan was the only coagulant.

Wastewater with cationic compounds

Figure 6 shows changes in the spectrum of wastewater with cationic compounds depending on the ferrous sulfate dose at a previously determined optimal dose of chitosan, i.e. 30 mg/dm3 (cf. ***Figure 2***). As seen from the data obtained, with an increasing dose of ferrous sulfate there was a gradual increase in the level of wastewater decolourisation. At the maximum dose of ferrous sulfate (1000 mg/dm3) the wastewater was completely decolourised.

Table 6 summarises results of colour determination in the wastewater (*DFZ*) and presents calculated levels of colour reduction after the coagulation process as compared to the wastewater before treatment.

The highest DFZ reduction was obtained at a dose of ferrous sulfate equal to 1000 mg/dm3, which was 95, 99 and 83% at wavelengths 436, 525 and 620 nm, respectively. Thus the wastewater was almost completely decolourised. Results of

Table 6. *Results of colour determination (DFZ) depending on the ferros sulfate dose at a chitosan dose of 30 mg/dm3 and calculated values of colour reduction after the coagulation process as compared to the wastewater before treatment. Initial DFZ at wavelength 436 nm – 104.3, 525 nm – 291.5, 620 nm – 17.0.*

Treatment parameters	Dose of ferrous sulfate (mg/dm3)				
	100	250	500	750	1000
DFZ in 1/m at wavelength					
436 nm	172.6	249.2	111.1	61.2	49.5
525 nm	440.7	652.5	254.4	81.8	39.1
620 nm	59.7	74.4	44.1	31.9	28.9
DFZ reduction in % at wavelength					
436 nm	83.5	76.1	89.3	94.1	95.2
525 nm	84.9	77.6	91.3	97.2	98.7
620 nm	64.8	56.2	74.0	81.2	83.0

Table 7. *Results of colour determination (DFZ) depending on the dose of ferrous sulfate at a chitosan dose of 100 mg/dm3 and calculated levels of colour reduction after the coagulation process in relation to the wastewater before treatment. Initial DFZ at wavelength 436 nm – 106.5, 525 nm – 3.0, 620 nm – 17.7.*

Treatment parameters	Dose of ferrous sulfate, mg/dm3				
	100	250	500	750	1000
DFZ in 1/m at wavelength					
436 nm	40.4	29.5	13.6	7.2	6.5
525 nm	9.7	71.4	27.1	7.9	5.5
620 nm	11.9	9.5	5.0	3.3	3.1
DFZ reduction in % at wavelength					
436 nm	62.0	72.3	87.2	93.2	93.9
525 nm	67.4	76.0	90.9	97.3	98.2
620 nm	32.8	46.5	71.8	81.2	82.4

the decolourization were much better (up to 20%) than in the case where chitosan was the only coagulant. The decolourisation of wastewater containing cationic compounds was very similar to that obtained in the wastewater comprising anionic chemicals.

Wastewater containing nonionic compounds

Figure 7 shows changes in the spectrum of wastewater containing nonionic compounds depending on the ferrous sulfate dose at a previously determined optimal dose of chitosan - 100 mg/dm^3 (cf. ***Figure 3***).

As can be seen from these data, with an increasing dose of ferrous sulfate there was a gradual increase in wastewater decolourisation. At maximum doses of ferrous sulfate (750 to 1000 mg/dm^3) the wastewater was completely decolourised.

Table 7 summarizes results of colour determination in the wastewater (*DFZ*) and presents calculated levels of colour reduction after the coagulation process in relation to the wastewater before treatment.

The highest *DFZ* reduction was achieved at a ferrous sulfate dose of 1000 mg/dm^3. At wavelengths 436, 525 and 620 nm it was 94, 98 and 82%, respectively. Hence the wastewater was practically completely decolourised. Results of the decolourisation were much better (up to 20%) than in the case of using chitosan as the only coagulant. The level of decolourisation of wastewater containing nonionic compounds was very similar to that which was obtained in the wastewater comprising anionic and cationic compounds.

Summary of results

The effects of decolourisation depended on the type of coagulant as well as on the composition and ionic nature of compounds present in the wastewater. When only chitosan was used, the model wastewater was better decolourized (up to 83 - 89%) than the real one (up to 63%). This was probably due to the more diversified composition of the real wastewater, which contained more different chemicals, including dyes. In the model wastewater the decolourization depended on the ionic nature of compounds present in the wastewater. When using chitosan as a coagulant, the best results of decolourisation were obtained in the wastewater containing nonionic compounds.

Additional use of ferrous sulfate besides chitosan in the coagulation processes improved the decolourisation of wastewater from 83 - 89% to 99%, and hence it was very beneficial. The wastewater after treatment was almost completely decolourised. In the case of a mixed coagulant (chitosan + ferrous sulfate) the effect of the ionic nature of compounds present in the wastewater on the decolourisation process was not important, and the resulting level of decolourisation reached 99% in all samples.

Optimal doses of chitosan providing good decolourisation of the wastewater ranged from 30 to 50 mg/dm^3, and were even 20 times lower than optimal doses of the mixed coagulant. From the viewpoint of sludge quantity it was much more favorable to use chitosan. Admittedly the sludge was finer than in the case of the mixed coagulant but its quantity was far smaller.

Selection of the most appropriate coagulant and its dose for the decolourisation of wastewater should be made individually taking into account the composition and ionic nature of contaminants as well as the amount of sludge formed.

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Received 25.06.2015 Reviewed 12.10.2015