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Removal of Pollutants from Textile Wastewater using Organic Coagulants

DOI: 10.5604/12303666.1221755

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Abstract
The aim of the study was to compare results of the treatment of different types of textile wastewater using selected organic, inorganic and mixed organic-inorganic coagulants and to assess their effectiveness. Results of the treatment depended on the coagulant type and on the composition and ionic nature of compounds present in the wastewater. The wastewater containing nonionic compounds was purified most efficiently, while that of anionic character was purified least effectively. The optimal doses of coagulants used in the treatment of a given type of wastewater were very different.

Key words: *textile wastewater, organic coagulants, decolourization, pollutants removal.*

Introduction

Wastewater from the textile industry is characterised by high environmental nuisance and toxicity. Typical of the wastewater is its intensive colour, high content of chemical substances, the presence of suspensions, poor biodegradability, high toxicity and different pH. For these reasons it is difficult to purify.

Coagulation is one of the methods to significantly reduce the concentration of pollutants in the wastewater. It is one of the easiest and least expensive methods of treatment, readily applicable in industrial plants. Coagulation allows for a significant 70-80% decolourisation of wastewater and a similar reduction in the concentration of organic compounds present in the wastewater. Coagulation is often carried out as the first step of treatment which is applied to remove the main bulk of organic pollutants from the wastewater. They are used both before discharging the wastewater to a receiving station or prior to further biological treatment, and when reusing the purified wastewater as a process water. In the latter case the processes of coagulation are necessary for further treatment of the wastewater by membrane or sorption methods [1, 2]. Advantages of the coagulation methods include high treatment efficiency, inexpensiveness, the easy availability of substrates, and they are simple procedures. A disadvantage of these methods is the formation of deposits which require further utilisation. The continuous interest in coagulation methods is confirmed by numerous papers which are published regularly in scientific and technical journals [3 - 5].

Two basic types of coagulants, inorganic and organic, are used in the coagulation processes. The first type includes primarily aluminium and iron salts: aluminium sulfate, iron sulfate and chloride [6, 7]. They may contain mineral additives such as calcium or calcium salts, and they require a certain pH to carry out the coagulation process effectively. The use of inorganic coagulants in textile wastewater is not particularly preferred because of the presence of heavy metal ions applied in wastewater treatment, which may cause difficulties in further treatment processes with the use of membrane methods. Additionally the presence of metal ions hampers the reuse of purified wastewater in dyeing and finishing processes [5].

It is more advantageous to apply organic coagulants, including the so-called polyelectrolytes, with different structures, which facilitate the formation and aggregation of deposits, thus accelerating the speed of sedimentation. The organic coagulants are water-soluble, mostly synthetic polymers, although some natural products are also used [8 - 12]. They are determined mainly according to their ionic structure as cationic, anionic, or nonionic. In textile wastewater particularly preferred is the application of cationic polyelectrolytes. This follows from the prevalence of anion-active compounds in textile wastewater, which further improves the effectiveness of the treatment. An additional advantage of the use of organic coagulants is a smaller dependence of treatment processes on pH, which makes the correction of the initial pH of wastewater unnecessary. After coagulation the content of dissolved metal ions is smaller [8]. Smaller quantities of coagulation sludge are often formed.

The use of only organic coagulants does not always improve the efficiency and effectiveness of coagulation. Sludge flocs are sometimes too fragile, tend to flocculate and sediment poorly. Thus the best solution is often the use of so-called mixed inorganic-organic coagulants containing aluminium or iron compounds and the addition of organic polymers [4, 7, 13, 14]. The use of mixed inorganic-organic coagulants brings numerous benefits, including, among others, the lowering of coagulant doses required, the formation of bigger sludge flocs, easier separation of sediments from the water phase, a smaller sludge volume, the possibility of carrying out the coagulation at lower temperatures, a lower pH of the process, and reduced concentration of iron or aluminium ions in water.

The aim of the study was to compare the results of treatment of different types of textile wastewater using selected organic, inorganic and mixed organic-inorganic coagulants and to assess their effectiveness.

Research methodology

Materials

The subject of research was model wastewater from cotton dyeing with reactive and direct dyes. It contained direct and reactive dyes, sodium chloride, acetic acid, sodium carbonate and anionic, cationic or nonionic auxiliaries. The different types of wastewater contained only auxiliary agents of a specific character, i.e. anionic, cationic or nonionic. The wastewater had an intensive red colour; its COD was from 320 to 402 mg O_2/dm^3, and the initial pH was 10.6.

The wastewater was subjected to treatment with organic coagulant Perrustol IPD and chitosan, mixed organic-inorganic coagulants Fercat and Alcat, and ferrous sulfate – an inorganic coagulant, for comparison.

The cationic organic coagulant Perrustol IPD is a product of condensation of fatty acids, while chitosan is a natural polymer – aminopolysaccharide obtained by chitin deacetylation.

The organic-inorganic coagulant Fercat (Chemical Plant KEMIPOL, Police, Poland) is iron(III) sulfate containing appropriate modifiers in the form of organic polyelectrolytes. The chemical composition comprises total iron in the amount of 11.60 to 12.00%, Fe^{+2} ions in the amount of 0.1 to 0.7%, and modifiers amounting to 10%.

The organic-inorganic coagulant Alcat (Chemical Plant KEMIPOL, Police, Poland) is an aqueous solution of polyaluminum chloride containing appropriate polyelectrolyte modifiers. The chemical composition comprises Al_2O_3 in the amount of 16.10 to 17.90%, Al^{+3} ions in the amount of 8.5 to 9.5% and organic polyelectrolyte modifiers amounting to 10%.

Methods and conditions of experiments

The process of coagulation was carried out in a beaker (volume 1.5 dm^3) by adding a specified dose of the coagulant to the wastewater. The doses of coagulants were from 0.5 to 2.5 g for Fercat, Alcat, Perrustol IPD and ferrous sulfate and from 0.05 to 0.25 g for chitosan. The volume of wastewater was 1 dm^3. The wastewater was stirred vigorously for about 2 minutes, and then slowly for another 10 minutes. After the precipitation of deposits, the solution was left undisturbed for 24 hours and then filtered, and wastewater samples were collected for analysis.

After the treatment, the colour of the wastewater samples was determined by the DFZ method [15]. 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

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

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

In the samples before and after the treatment, COD was determined by Hach-Lange tests [16].

Experimental equipment

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

Results and discussion

An optimal dose was the one at which the reduction in pollution was the highest [17].

Wastewater containing anionic surfactants

Figure 1 shows changes in the colour reduction (DFZ) and COD in the wastewater containing anionic surfactants depending on coagulant doses.

Fercat coagulant

As follows from the data, in the case of Fercat – the mixed organic-inorganic coagulant, the pollutant reduction rate increased with an increasing dose of the coagulant (***Figure 1.a***). The reduction in COD ranged from 19% at a dose of 0.5 g/dm^3 to 37% at a dose of 2.5 g/dm^3. An optimal dose was 2 g/dm^3, at which a 39% reduction in COD was obtained. The colour reduction increased in the range from 50 to 89%. Thus the wastewater was well discoloured.

Alcat coagulant

In the case of Alcat the treatment gave better results, expressed as COD reduction from 23 to 44% (***Figure 1.b***). The optimal dose at which the highest COD reduction was reached was 1 g/dm^3. Colour removal in the wastewater was higher, from 74 to 95%. Consequently the wastewater was very well discoloured. In contrast to Fercat, better results of treatment were achieved at the lowest doses of Alcat applied.

Perrustol IPD coagulant

When using the organic coagulant Perrustol IPD, irrespective of the dose, a quite similar reduction in COD (about 23%) and colour (about 65%) was obtained (***Figure 1.c***). The reduction in impurities practically did not depend on the dose of coagulant. Therefore the optimal dose was the lowest of those applied, i.e. 0.5 g/dm^3.

Chitosan coagulant

In the case of chitosan the doses applied were smaller by one order than the those of other coagulants (***Figure 1.d***). At the lowest coagulant doses the reduction in COD was up to 10%. At higher doses the COD increased, which indicated the dissolution of the coagulant in the wastewater. In general, the COD reduction was slight, whereas wastewater decolourisation was very high, reaching 80 - 90%.

Ferrous sulfate coagulant

When using a classical inorganic coagulant, i.e. ferrous sulfate, the degree of pollutant reduction increased with an increasing dose from 10 to 39% (***Figure 1.e***), where an optimal dose was 2 g/dm^3. Colour reduction was very high, reaching from 72 to 100%.

Figure 2 shows individual coagulant doses at which the highest reduction in colour and COD in anionic wastewater was obtained.

As can be seen, the best results of decolourisation were obtained in the case of ferrous sulfate, while the highest COD reduction was reached for Alcat. It should be noted, however, that the dose of ferrous sulfate was big, reaching 2 g/dm^3. Slightly worse decolourisation of the wastewater was obtained in the case of chitosan, but the dose of this coagulant applied was 40 times smaller. In the case of COD reduction the best results were obtained with the use of Alcat, where the dose applied was 2 times lower than that of Fercat or ferrous sulfate.

Figure 3 shows the different sizes of optimal doses of coagulants used in

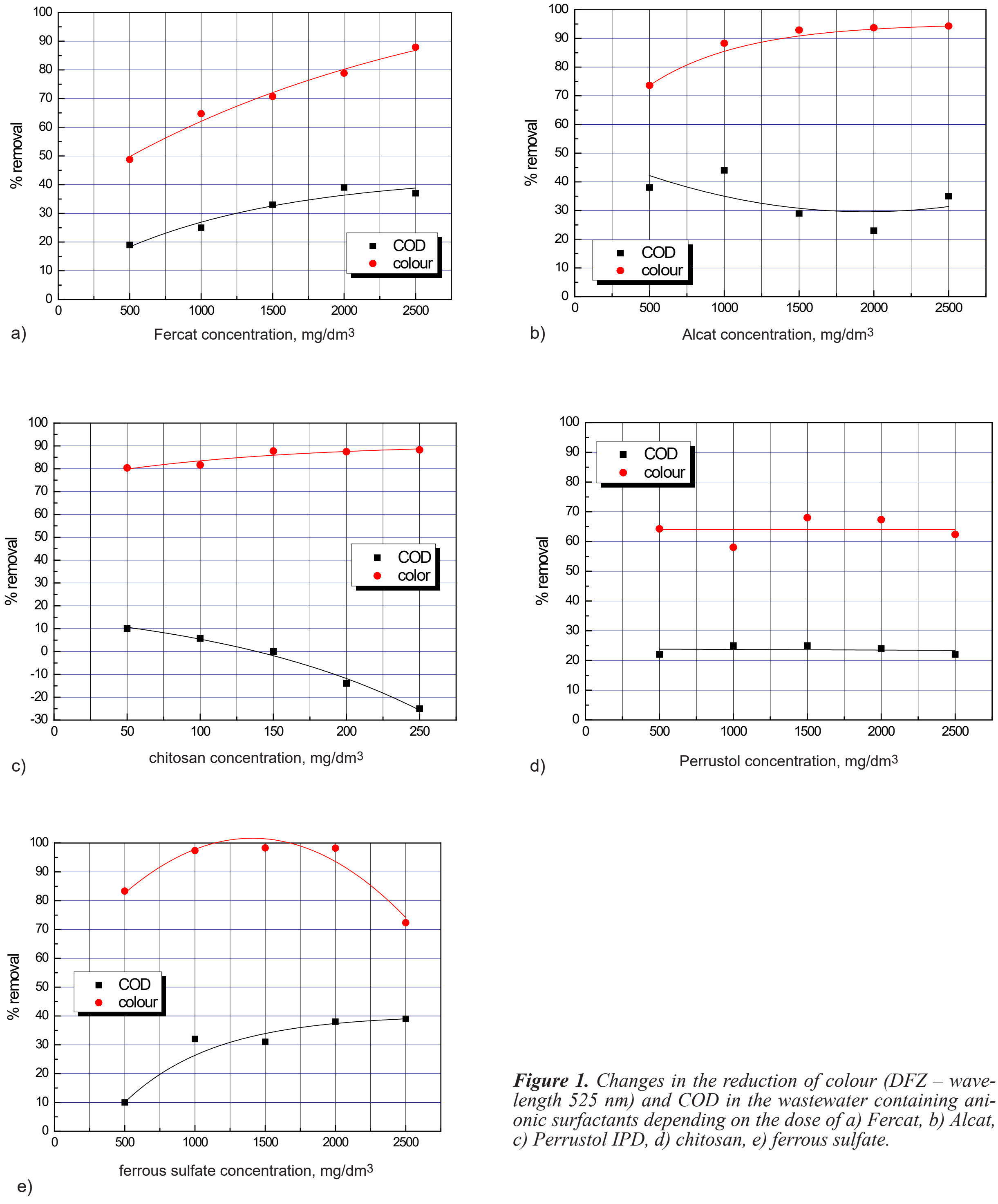

Figure 1. *Changes in the reduction of colour (DFZ – wavelength 525 nm) and COD in the wastewater containing anionic surfactants depending on the dose of a) Fercat, b) Alcat, c) Perrustol IPD, d) chitosan, e) ferrous sulfate.*

the treatment of textile wastewater containing anionic surfactants.

Wastewater containing cationic surfactants

Figure 4 shows changes in the reduction in colour (DFZ) and COD in wastewater containing cationic surfactants depending on coagulant doses.

Fercat coagulant

As follows from the data, in the case of Fercat, a mixed organic-inorganic coagulant, the rate of pollutant reduction increased with the increasing coagulant dose (***Figure 4.a***). The reduction in COD was in the range from 55% at a dose of 0.5 g/dm^3 to 61% at a dose of 2 g/dm^3. An optimal dose was 1.5 g/dm^3, at which a 61% decrease in COD was obtained. The colour reduction increased in the range from 70 to 90%. Thus the wastewater was well decolourised.

Alcat coagulant

In the case of mixed coagulant Alcat, the results of treatment were similar to those obtained for Fercat (***Figure 4.b***). They were expressed by a COD reduction from 46 to 61%. The optimal dose

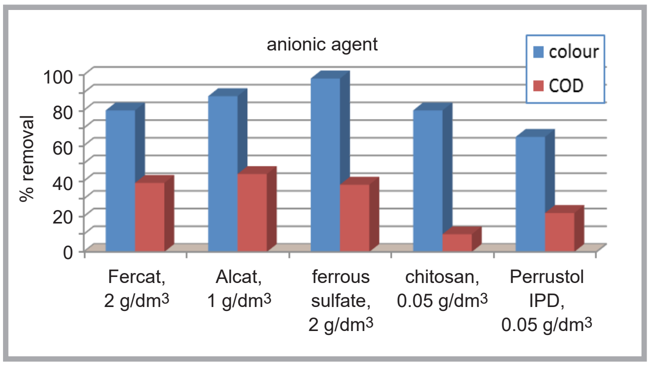

Figure 2. Individual coagulant doses at which the maximum reduction in colour and COD in wastewater containing anionic surfactants was achieved.

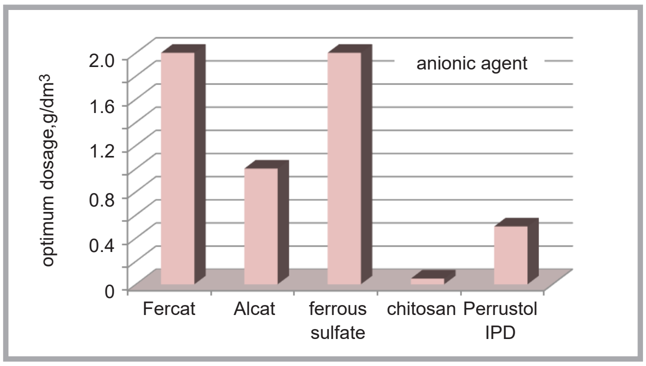

Figure 3. Optimal doses of individual coagulants used for the treatment of wastewater containing anionic surfactants.

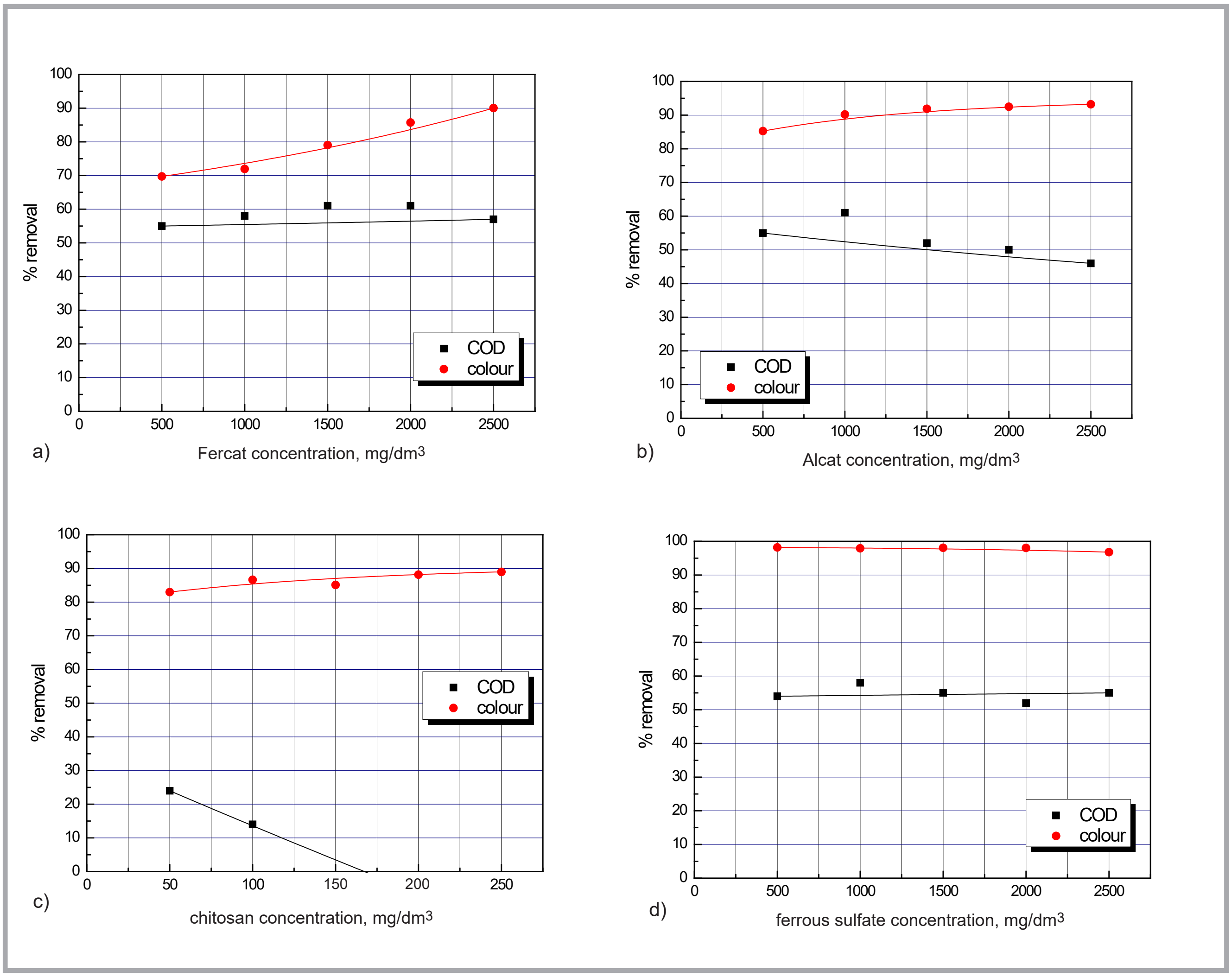

Figure 4. Changes in the reduction of colour (DFZ, wavelength 525 nm) and COD in wastewater containing cationic surfactants depending on the dose of a) Fercat, b) Alcat, c) chitosan, d) ferrous sulfate.

at which the highest COD reduction was obtained was 1 g/dm^3. The degree of wastewater decolourisation was higher and amounted to from 85 to 93%. Thus the wastewater was very well decolourized. In contrast to Fercat, better results of treatment were obtained at the lowest doses of Alcat applied.

Chitosan coagulant

When using the organic coagulant chitosan, doses smaller by one order than those of the other coagulants were applied (***Figure 4.c***). At the smallest doses of the coagulant the reduction in COD was up to 24%. At bigger doses the COD increased, which indicated that the coagulant dissolved in the wastewater.

Ferrous sulfate coagulant

While using the classical inorganic coagulant ferrous sulfate, the reduction in pollutants was fairly similar in the range of doses applied, reaching from 52 to 58% (***Figure 4.d***). An optimal dose was 1.5 g/dm^3. Colour reduction was very high, amounting to 97 - 99%.

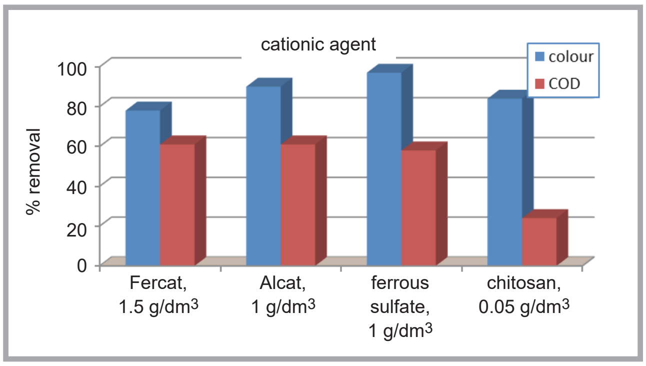

Figure 5. Doses of individual coagulants at which the maximum reduction in colour and COD in wastewater containing cationic surfactants was achieved.

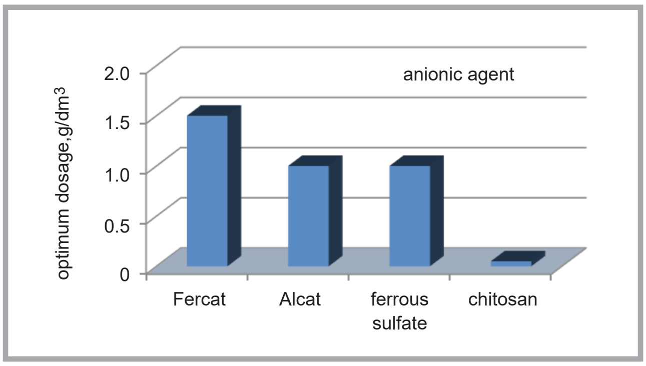

Figure 6. Optimal doses of individual coagulants used in the treatment of wastewater containing cationic surfactants.

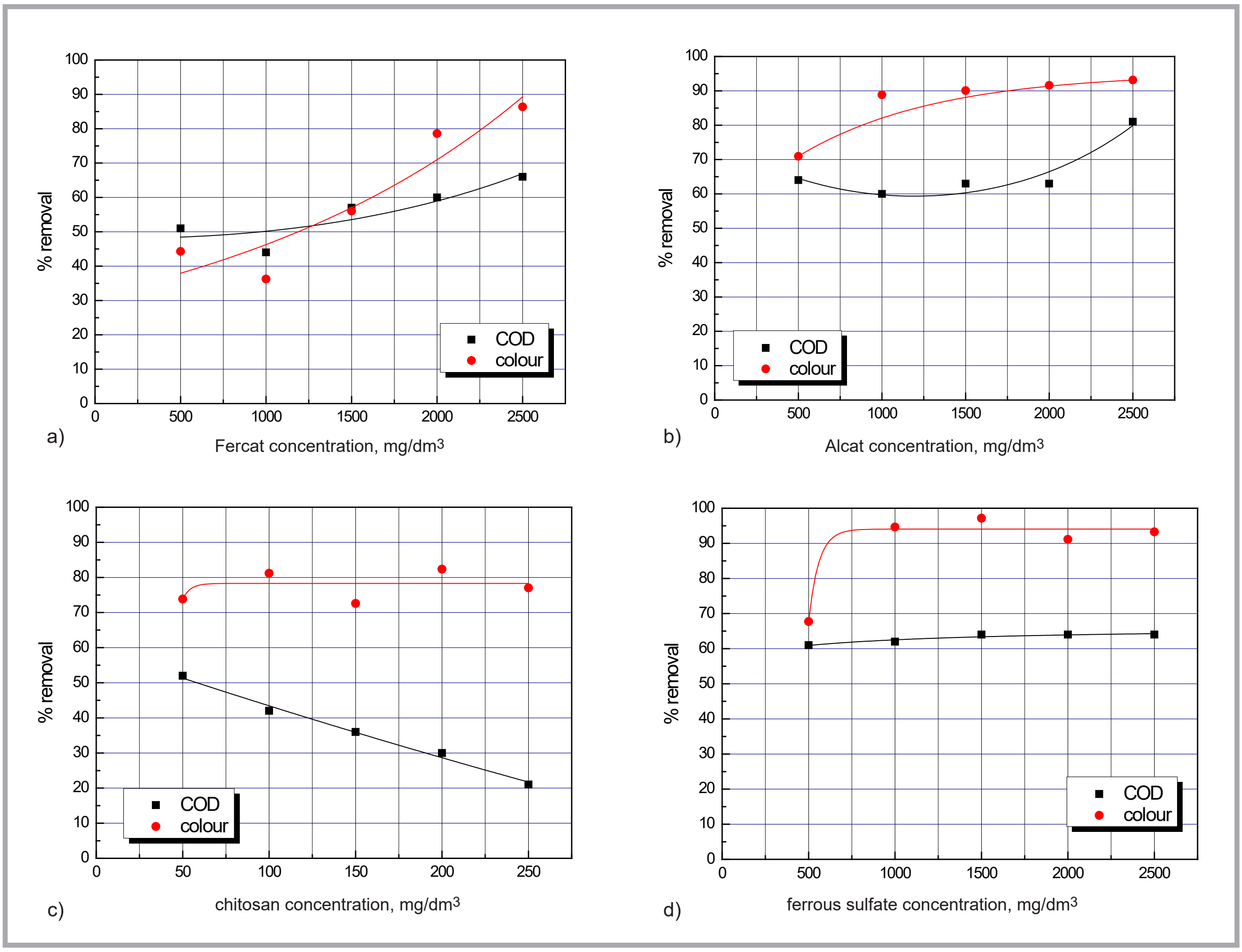

Figure 7. Changes in the removal of colour (wavelength 525 nm) and COD in wastewater containing nonionic surfactants depending on the doses of a) Fercat, b) Alcat, c) chitosan, d) ferrous sulfate.

Figure 5 shows doses of individual coagulants at which the highest reduction in colour and COD in the wastewater with cationic surfactants was obtained.

As can be seen, the best results of decolourization were obtained in the case of ferrous sulfate and Alcat when colour removal in the wastewater was 98 and 90%. However, noteworthy are the results of wastewater decolourization with the use of chitosan. The degree of wastewater decolourization reached 80%, whereas the dose of chitosan required was 20 times less than when using other coagulants. In the wastewater containing cationic surfactants the reduction in COD reached 60%,higher than in the case of wastewater which contained anionic surfactants when COD reduction reached 40%. Additionally the coagulant doses required were lower, ranging from 1 to 1.5 g/dm^3.

Figure 6 shows optimal doses of coagulants used in the treatment of textile wastewater containing cationic surfactants.

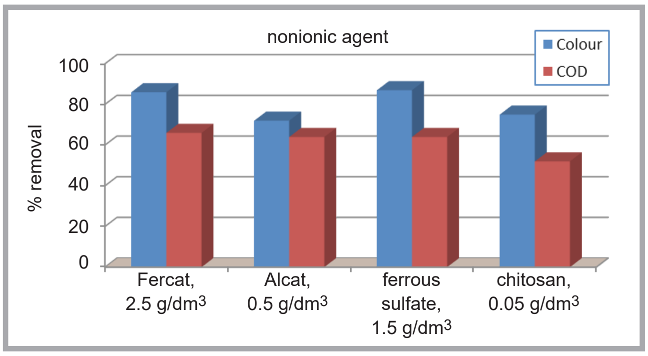

Figure 8. Doses of individual coagulants at which the maximum reduction in colour and COD in wastewater containing nonionic surfactants was achieved.

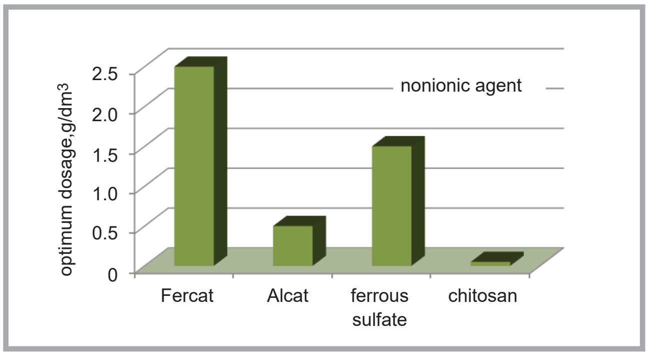

Figure 9. Optimal doses of individual coagulants used for the treatment of wastewater containing nonionic surfactants.

Wastewater containing nonionic surfactants

Figure 7 illustrates changes in the reduction in colour (DFZ) and COD in wastewater containing nonionic surfactants depending on coagulant doses.

Fercat coagulant

As follows from the data quoted, in the case of using the mixed organic-inorganic coagulant Fercat, the reduction in pollutants increased with an increasing coagulant dose (***Figure 7.a***). The reduction in COD ranged from 51% at a dose of 0.5 g/dm^3 to 66% at 2.5 g/dm^3. An optimal dose was 2.5 g/dm^3 , at which a 66% decrease in COD was obtained. Colour reduction increased from 38 to 88%. Thus the wastewater was well decolourized.

Alcat coagulant

In the case of the mixed coagulant Alcat, the reduction in COD was much higher than in the case of Fercat, reaching from 60 to 81% (***Figure 7.b***). An optimal dose was 2,5 g/dm^3. Also colour removal was higher, ranging from 71 to 93%. Hence the wastewater was very well decolourized.

Chitosan coagulant

When using the organic coagulant chitosan, doses smaller by one order than the those of other the coagulants were applied (***Figure 7.c***). At the smallest doses of the coagulant the reduction in COD was up to 52%. At higher doses the COD reduction decreased, which could be related to the partial dissolution of chitosan in the wastewater. In general, the COD reduction was satisfactory. Colour removal was high, reaching 72 - 82%.

Ferrous sulfate coagulant

When using the classical inorganic coagulant ferrous sulfate, the reduction in pollutants was very similar, in the range of doses applied of 61 - 64% (***Figure 7.c***). Therefore the optimal dose was the lowest used, i.e. 0.5 g/dm^3. Colour removal was high, reaching 67 - 97%.

Figure 8 shows doses of individual coagulants at which the highest reduction in colour and COD in wastewater with nonionic surfactants was obtained.

The best results of decolourization were obtained in the case of ferrous sulfate and Fercat, where colour removal exceeded 80%, while being slightly worse, reaching 70 - 75%, when Alcat and chitosan were applied. It should be noted, however, that also in the case of wastewater containing nonionic surfactants does decolourization require the smallest chitosan dose, which was from 10 to 50 times lower than that of the other coagulants applied. In the case of all coagulants the reduction in COD was fairly uniform, reaching about 60%, except for chitosan, where it did not exceed 50%. However, the doses required were greatly varied, and, for instance, for Alcat (0.5 g/dm^3) they were 3 and 5 times lower than for ferrous sulfate and Fercat, respectively.

Figure 9 illustrates optimal doses of coagulants used in the treatment of textile wastewater containing nonionic surfactants.

For comparison, in the literature, authors achieved a removal of colour from 50 to 97% and that of COD from 28 to 73% for real textile wastewater treated with mixed organic-inorganic coagulants [17].

Conclusions

The results of treatment depended on the type of coagulant applied as well as on the composition and ionic nature of compounds present in the textile wastewater. The best purified was the wastewater containing nonionic compounds, while the least was the anionic wastewater. In general, in all cases good or very good decolourisation of wastewater was obtained. The optimal doses of coagulants used in the treatment of individual types of wastewater were very different.

The lowest optimal doses were obtained for the organic coagulant chitosan. The optimal dose of chitosan was at least an order of magnitude lower, up to even 40 times, compared to those of the other coagulants. This coagulant reduced the colour of wastewater well, but the reduction of COD was small, especially in the nonionic wastewater. Relatively low doses were sufficient when using Alcat – a coagulant of mixed organic-inorganic nature. On the other hand, much higher doses were required when ferrous sulfate (inorganic coagulant) or Fercat (mixed organic-inorganic coagulant) was used.

Selection of the most appropriate coagulant, as well as its dosage should be determined individually, taking into account the composition and ionic character of contaminants present in the wastewater and the types of components to be removed.

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Received 07.05.2015 Reviewed 09.05.2016