ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 35 no. 1 pp. 33 - 43 2009

PL ISSN 0324-8461

ROLE OF RECYCLED SLUDGE AGE IN COAGULATION OF COLORED WATER

JOLANTA GUMIŃSKA, MARCIN KŁOS

Silesian University of Technology, Faculty of Energy and Environmental Engineering, Institute of Water and Wastewater Engineering
ul. Konarskiego 18, 44-100 Gliwice, Poland
e-mail: jolanta.guminska@polsl.pl, marcin.klos@polsl.pl

Keywords: Optimum coagulant dose, recirculation, post-coagulation sludge.

Abstract: All multifunctional units combine flocculation and sedimentation to improve efficiency of treatment process. The characteristic feature of the unit is a contact of raw water with previously generated flocs which enhances flocculation by increasing interparticle collisions and sorption ability of flocs. On the basis of the authors' experience it was stated that in spite of significant differences between the procedure of conventional treatment and treatment in multifunctional units, an optimum coagulant dose is determined in jar testing which is commonly used for conventional treatment. The influence of sludge recirculation is not taken into consideration resulting in reagent overdosing. In this paper the results of the research on coagulation with post-coagulation sludge recirculation in aspect of sludge age are presented. It was stated that for the tested water, sludge recirculation may result in significant lowering of optimum alum doses provided that a proper degree of fresh sludge recirculation is applied.

INTRODUCTION

In water treatment the process of coagulation is applied to remove colloidal dispersed minerals and natural organic substances in a dissolved or colloidal form. Organic impurities found in natural waters are mainly humic substances which cause yellow or brown color of the waters. These organics are undesirable by consumers not only because of aesthetic reasons. The most important is the fact that they negatively influence water quality in a distribution system. This influence may be direct, when organics while chlorinated may be the source of carcinogenic trihalomethans or indirect, when they decrease biological stability of water, being nutrients for microorganisms.

However, in waterworks practice most of water treatment plants are optimized mainly for the removal of impurities which cause turbidity, not for minimization of a required disinfectant dose [5, 13]. It is caused by the fact that in the majority of cases it is more difficult to decrease turbidity of water after rapid filters to the desired level (0.1–0.2 NTU), taking into account Cryptosporidium oocyst presence, than to lower concentration of organic matter measured as TOC (Total Organic Carbon) to a value 5 mg C/dm^3. Usually technological parameters for required turbidity removal stated by the operators of a treatment system meet quality requirements in the aspect of organics content. However, if organics' contamination of water is considered as a source of DBP (Disinfection By-Products) on the one hand and a source of assimilable organic carbon (AOC) on the other, the concentration of organic matter in water after treatment may be still too high.

According to many authors variable effectiveness of turbidity and NOM (Natural Organic Matter) removal at a given configuration of flocculation parameters results from the fact that optimum technological conditions for the removal of turbidity are different from these for NOM [1–4, 6, 10, 15]. The basic parameters influencing the coagulation of humic substances are a coagulant dose and the pH at which treatment is carried out. Narkis and Rebhun [14] found that the presence of organic matter in solution or as a complex with the mineral clay particle inhibits the process of flocculation. So those to make flocculation possible, large doses of flocculant are required. According to a number of studies [7, 8, 12] the optimum pH for color removal with alum is noted to be in the range of 5–6.5. According to Kim *et al.* [13] turbidity and TOC removal regions mostly overlap. The difference is only in the restabilization region which is wider for turbidity removal than for TOC removal. Hence, it may be concluded that most TOC is removed together with turbidity.

The processes of coagulation and separation of post-coagulation solids may be run in various technological systems. If the system consists of a rapid mix tank, followed by a flocculator and then a sedimentation basin, a treatment process is called conventional coagulation. Conventional treatment plant requires a large area to construct tanks for mixing, flocculation and sedimentation resulting in high investment and exploitation costs of the system. So that, to make the process more effective, flocculation and sedimentation may be run in one device [9]. All multifunctional units combine flocculation and sedimentation to enhance efficiency of treatment process by using the recirculation of sludge. The role of sludge recirculation is to accelerate agglomeration of freshly produced flocs and to increase sorption capacity of flocculated sludge solids. One of crucial factors which decide about a proper coagulation course in this type of unit is a coagulant dose. However, no research on the influence of suspended sludge on treatment effectiveness has been done. A coagulant dose for coagulation in a multifunctional unit is determined in jar testing which is commonly used for conventional treatment. It means that a dose determined in this way is not optimal, because when using this method the influence of sludge is not taken into consideration.

This paper focuses on the possibility to enhance coagulation by post-coagulation sludge recirculation and to decrease an optimum coagulant dose in aspect of sludge age. The influence of recirculation degree on treatment effectiveness was also presented.

MATERIALS AND METHODS

Water sample

Water sample was prepared by mixing peat extract with tap water to simulate colored water sample. The peat was separated by utilizing differences in solubility at different pH values. A stock solution of humic substances was obtained by extraction with 0.1 N sodium hydroxide. After 1 week ageing the clarified solution of humic acids was collected. Test samples were prepared by diluting the stated volume of aquatic humic extract in 0.7 dm^3 of tap water with the corresponding apparent color of 80–90 mg Pt/dm^3 (true color of 70–80 mg Pt/dm^3). Color was determined spectrophotometrically according to the producer method. Because the results of color measurements after treatment in filtered and unfiltered samples were very close and the difference was not higher than 5%, it was decided to make measurements only in unfiltered samples, i.e. apparent color. Absorbance UV in unfiltered samples at the wavelength 254 nm (it is commonly used as an indicator of organic contaminants in water) was in the range of 21.76–24.86 m^{-1}. Absorbance UV_{254} measurements of samples filtered through 0.45 μm membrane filter were in the range of 84–90% of the values noted in unfiltered samples. It means that most of organic substances were in a dissolved form. Aluminium concentration in raw water did not exceed 0.2 mg Al/dm^3 and was in the range from 0.15–0.17 mg Al/dm^3, which is an acceptable value in drinking water. Turbidity didn't exceed 1 NTU. So that, to prepare homogeneous sample while extract diluting it was mixed at 200 rpm for 120 s.

Preparation of coagulant solution

The stock solution of alum was prepared by dissolving $Al_2(SO_4)_3 \cdot 18H_2O$ in D.I. water to obtain 2% concentration. Coagulant doses reported in this study are presented in mg Al/dm^3.

Apparatus

A Carl Zeiss UV/VIS spectrophotometer was used for all absorbance measurements. Measurements were carried out in a 20 mm quartz cuvette. Color was measured with a photometer Nanocolor (MECHERY NAGEL). The mixing device was a six-beaker Flocculator SW1 (Stuart Scientific).

JAR TESTS

Fresh sludge recirculation

The research consisted of four stages. In the first stage jar tests were performed to evaluate an optimum coagulant dose. Rapid-mixing for 1 min at rotational speed of 200 rpm was followed by 30-min slow-mixing at 30 rpm. After settling for 30 min residual color, absorbance UV_{254}, turbidity and dissolved aluminium (residual coagulant) of the supernatant were measured. All experiments were carried out at pH = 6.9–7.2. The optimum coagulant dose was the lowest one which allowed to gain high treatment effectiveness and higher doses did not allow to achieve significant improvement of water quality.

In the second stage the optimum coagulant dose was injected into six beakers to produce sludge. After coagulation and settling at the operational parameters stated in the first stage of the study the supernatant was removed and the stable volume of sludge from each beaker was collected into one beaker. The collected sludge was immediately used in the third stage of the experiment.

In the third stage the treatment process was conducted at six coagulant doses as follows: 20%, 30%, 50%, 70%, 90% and 100% of the optimum dose stated in the first stage. After 1-min rapid-mixing the rotational speed was decreased from 200 to 60 rpm. At the lower speed, which was held for 2 min, the stated volume of fresh sludge (collected in the second stage) was injected into the first five beakers, where coagulant doses were lower than the optimum one. The purpose of speed lowering, while sludge mixing with water, was to prevent sludge flocs from breaking-up. The sixth beaker (with the optimum dose of coagulant) was a comparative one and no sludge was injected into it. After sludge injection the speed was decreased again to 30 rpm and 30-min flocculation started. The sludge was added in the amount 20 cm^3 and 40 cm^3 in the first and second series, respectively. Taking into consideration the fact that water samples were 0.7 dm^3 the volume degree of recirculation was 2.9% and 5.7%. Similarly to the first stage of the study, after flocculation and settling for 30 min residual color, absorbance UV_{254} and aluminium of supernatant were measured.

The fourth stage was a comparative one. At that stage conventional coagulation process and settling (rapid-mixing for 1 min at 200 rpm, 30-min slow-mixing at 30 rpm, settling for 30 min) was run with coagulant doses applied in the previous stage (20%, 30%, 50%, 70%, 90% and 100% of the optimum dose) but without sludge recirculation.

Aged sludge recirculation

The aim of the research was to study the influence of the age of post-coagulation sludge on treatment effectiveness. The studies were conducted according to the same method as applied in the series where fresh sludge was recycled. However, instead of fresh sludge, the sludge after 1-day or 6-day ageing was used.

RESULTS AND DISCUSSION

Influence of recirculation degree on treatment effectiveness

According to the stated method the testing was conducted for two different recirculation degrees: 2.9% and 5.7%. The optimum alum dose stated at the first stage was 3 mg Al/dm^3. The residual color at that dose was 20 mg Pt/dm^3 (75% of color removal). Residual UV absorbance was 9.21 m^{-1} (57.7% removal). The results of treatment effectiveness in these series are presented in Figures 1–4. In the analyses residual color and absorbance changes were taken into consideration. The results show that sludge recirculation causes distinct decrease in the optimum alum dose. When 20 cm^3 of sludge (2.9% recirculation degree) was added with the coagulant dose of 1.5 mg Al/dm^3 absorbance removal was 57.2% with corresponding residual color 25 mg Pt/dm^3 (Figs. 1 and 2.). This effectiveness was similar to the effectiveness of treatment achieved in the stage without sludge recirculation but at the dose twice higher, i.e. 3 mg Al/dm^3. The results of treatment without sludge recirculation at the dose of 1.5 mg Al/dm^3 were much worse in comparison to the process with sludge addition. Absorbance was decreased only by 22%; residual color was noted at 60 mg Pt/dm^3. With increase of alum dose the better effects of coagulation with sludge recirculation were observed. At 70% of the optimum coagulant dose the quality of treated water with sludge addition was even better (67.3% of absorbance removal, 15 mg Pt/dm^3 of residual color) than the quality achieved in conventional treatment at the optimum dose.

The increase in the amount of recycled sludge to 40 cm^3 (5.7% recirculation degree) caused more significant effects on the contaminants removal (Figs. 3 and 4). The results indicate that sludge recirculation enhances coagulation and treatment is more effective than in conventional coagulation, even if the alum dose is much lower than the optimum one. Figures 3 and 4 show that at 30% of the optimum dose i.e. 0.9 mg Al/ dm^3 and sludge injection the effectiveness of organic matter removal (59.8% of absorbance removal, 20 mg Pt/dm^3 of residual color) was similar to the results of conventional coagulation (stage 1) but at a much higher dose (3 mg Al/dm^3). When a dose of 0.9 mg Al/dm^3 was applied

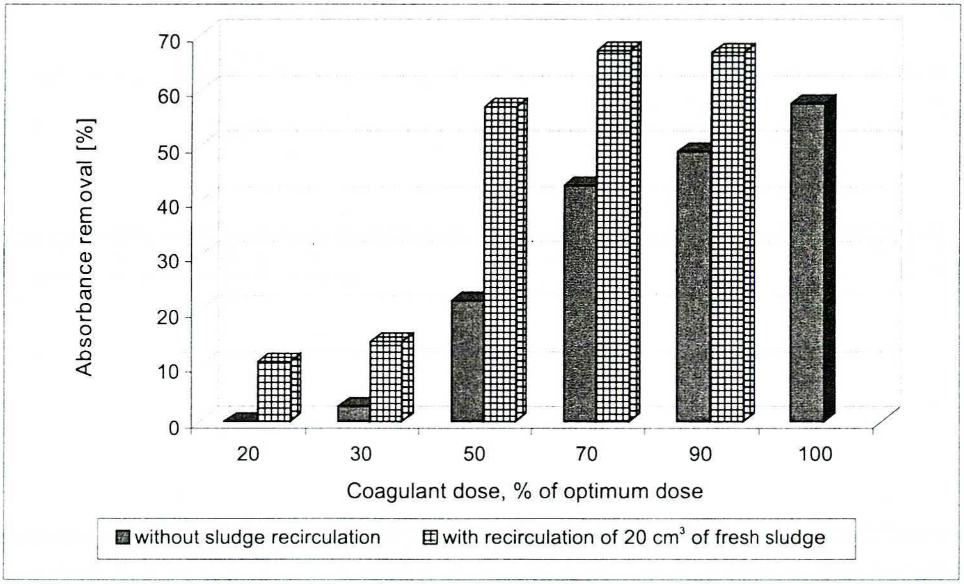

Fig. 1. Effectiveness of coagulation with recirculation of 20 cm^3 of fresh sludge (absorbance removal)

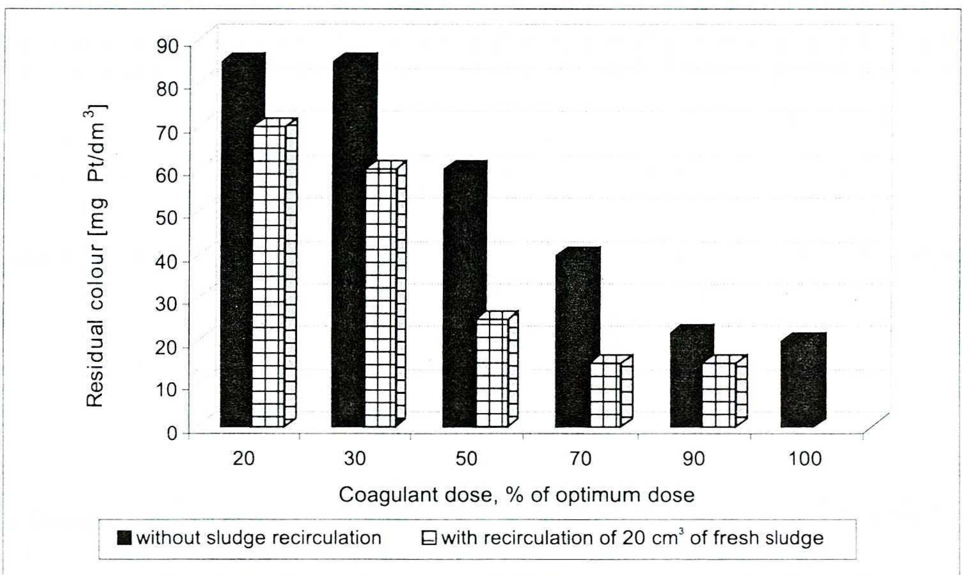

Fig. 2. Effectiveness of coagulation with recirculation of 20 cm^3 of fresh sludge residual color)

conventional coagulation was totally ineffective. The residual color was at the same value as in raw water. The increase of a coagulant dose to 1.5 mg Al/dm^3 during coagulation with sludge injection resulted in 65.9% of absorbance removal and 15 mg Pt/dm^3 of residual color. At the same alum dose coagulation without sludge recirculation resulted only in 22% of absorbance removal and residual color 60 mg Pt/dm^3. Taking into consideration the conventional coagulation effectiveness at the dose of 3 mg Al/dm^3 it may be concluded that the sludge addition may not only allow to decrease an alum dose but may also improve water quality after treatment in comparison to the effects of conventional coagulation at the optimum process parameters. In the tested range of coagulant doses, besides the lowest one, absorbance UV_{254} values in filtered samples were 47.3–49.5% and 53.2–66.7% of values noted for unfiltered samples for conventional coagulation and with

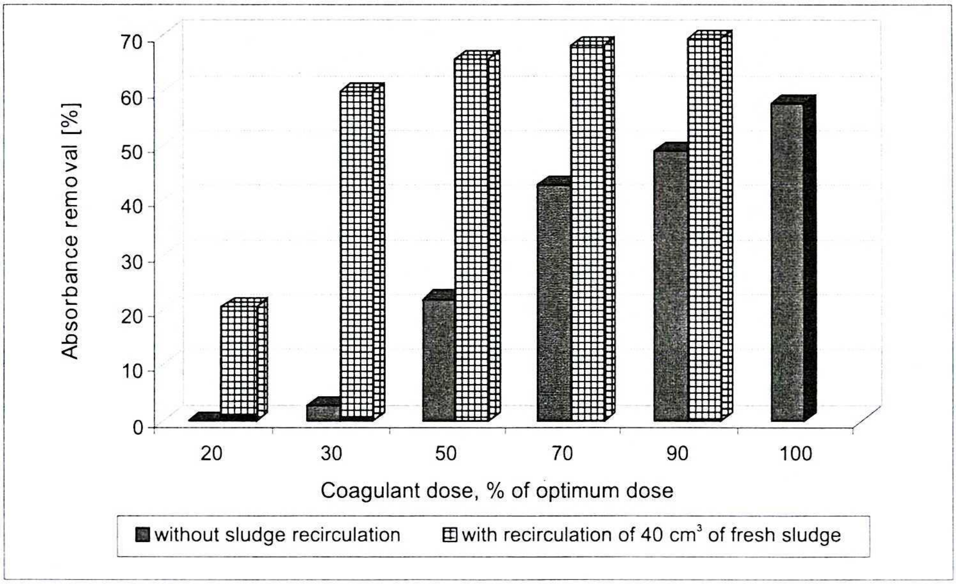

Fig. 3. Effectiveness of coagulation with recirculation of 40 cm^3 of fresh sludge (absorbance removal)

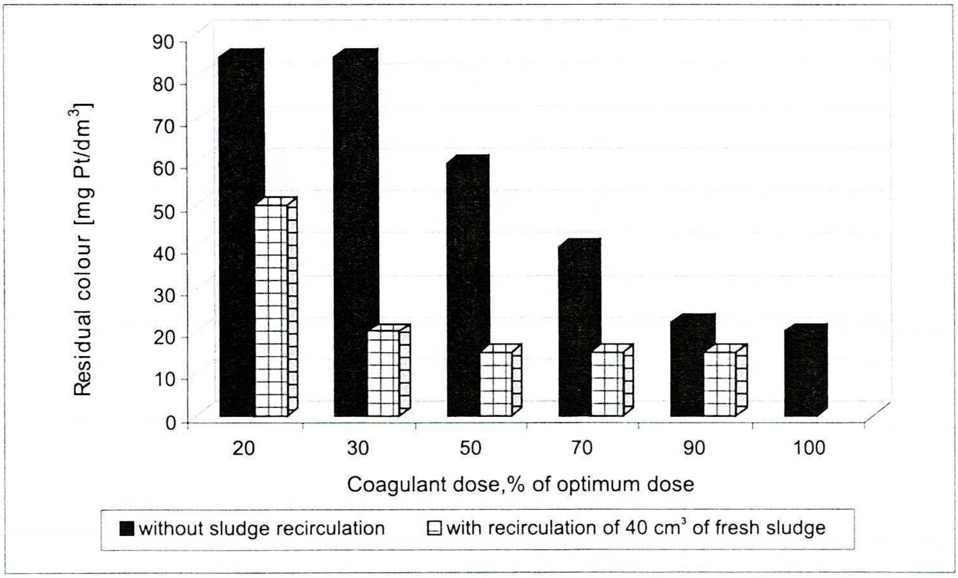

Fig. 4. Effectiveness of coagulation with recirculation of 40 cm^3 of fresh sludge (residual color)

sludge recirculation, respectively. At 30% of the optimum alum dose without sludge injection real values were 21.15 m^{-1} and 10 m^{-1} in unfiltered and filtered water. When sludge was added 9.28 m^{-1} and 4.44 m^{-1} values respectively, were measured. In this case sludge addition improved sorption ability and enhanced agglomeration of generated flocs. At higher alum doses both in samples collected after coagulation with and without sludge recirculation values of absorbance in filtered samples were close. It means that at this range of doses for the tested water sludge recirculation mainly improves flocs agglomeration and this way accelerates solids separation in sedimentation process. In all samples where alum doses were not below 30% of the optimum one the concentration of residual coagulant was very low and did not exceed the value of 0.2 mg Al/dm^3. Thus the aluminium concentration resulted from added coagulant was only 0.03–0.05 mg Al/dm^3.

Fresh sludge injection during flocculation may improve the process effectiveness and decrease coagulant dose, even three times. However, the condition of such effects is that treatment is run with proper recirculation degree. For the tested water such effects were achieved at 5.7% recycle ratio. On the other hand, the effectiveness is strictly connected with raw water quality and the treatment results are not always so significant [11]. The purposefulness of recirculation should always be proceeded by research.

Influence of sludge age on treatment effectiveness

The studies of the influence of post-coagulation sludge age on treatment effectiveness were made for 5.7% recirculation degree. At this degree, in the series when fresh sludge was applied, the best effects were achieved. In Figures 5 and 6 the results for 1-day-old sludge are presented. The optimum coagulant dose was stated at the same value as in the previous series, i.e. 3 mg Al/dm^3, but the quality of water after treatment was better (63% of absorbance removal and 15 mg Pt/dm^3 of residual color). The probable reason of different results achieved in both series at the same coagulant dose may be explained by changes of tap water parameters not being under control. The analysis of the results for 1-day sludge indicates that there is significant deterioration in treatment effectiveness when aged sludge is injected. It was impossible to produce water of better quality than in conventional coagulation at the optimum coagulant dose. Though, it was noticeable that at coagulant doses, lower than optimal one, sludge addition enhanced treatment in comparison to conventional coagulation run at the same reagent doses. For example, at the dose of 1.5 mg Pt/dm^3 (50% of the optimum dose) in conventional coagulation no changes of absorbance after treatment were noted, while at the same dose with 5.7% sludge recirculation 19.3% decrease of absorbance value was measured. Residual color of samples obtained after treatment both with and without sludge recirculation was 60 mg Pt/dm^3. The effectiveness close to that noted during conventional coagulation at the optimum coagulant dose (3 mg Al/dm^3) was observed at 90% of the optimum dose with sludge recirculation resulting in 60.3% organic matter as absorbance removal and color at 20 mg Pt/dm^3 were noted. Such results suggest that treatment with 1-day post-coagulation sludge recirculation is ineffective and economically unexplainable for the water tested in these investigations.

Figures 7 and 8 present results for 6-day sludge. The analysis of samples after coagulation, with and without sludge recirculation, at the same coagulant doses, indicates that sludge addition may cause deterioration in water quality after treatment, e.g. at 30% of the optimum alum dose.

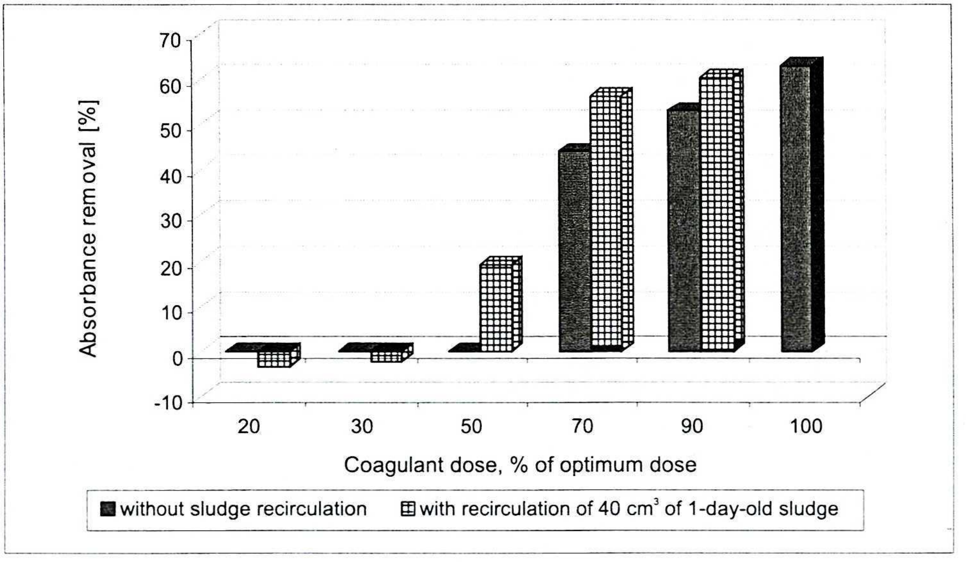

Fig. 5. Effectiveness of coagulation with recirculation of 40 cm^3 1-day-old sludge (absorbance removal)

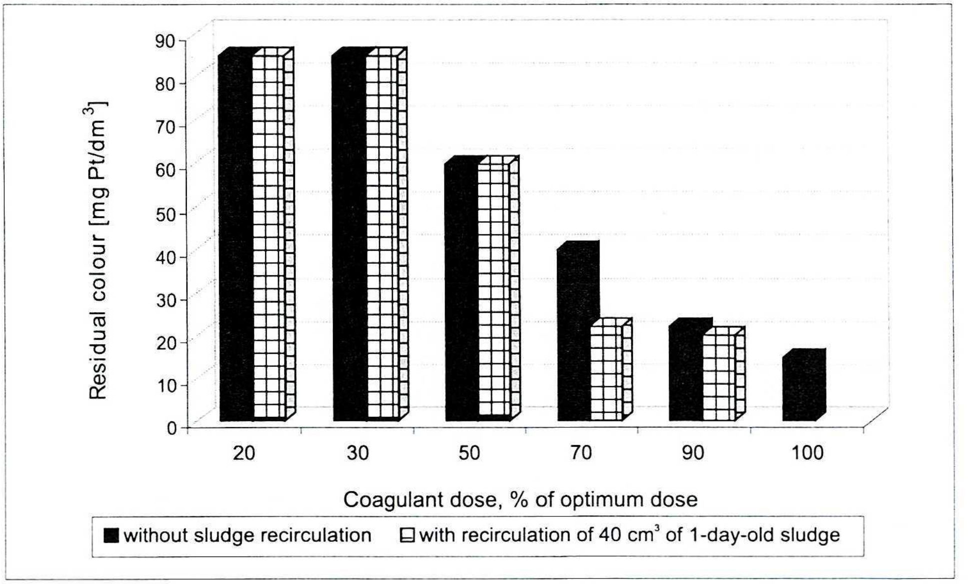

Fig. 6. Effectiveness of coagulation with recirculation of 40 cm^3 1-day-old sludge (residual color)

In samples where fresh sludge was added absorbance values decreased with the decrease of color. Comparing the results of treatment for 1-day and 6-day-old sludge besides differences in effectiveness, different behavior of absorbance and color was observed. When 1-day sludge was injected at 20% and 30% of the optimum alum dose any removal of color and noticeable changes of absorbance were noted. A little increase of absorbance values resulted from coagulant addition, which in this case, caused only the increase

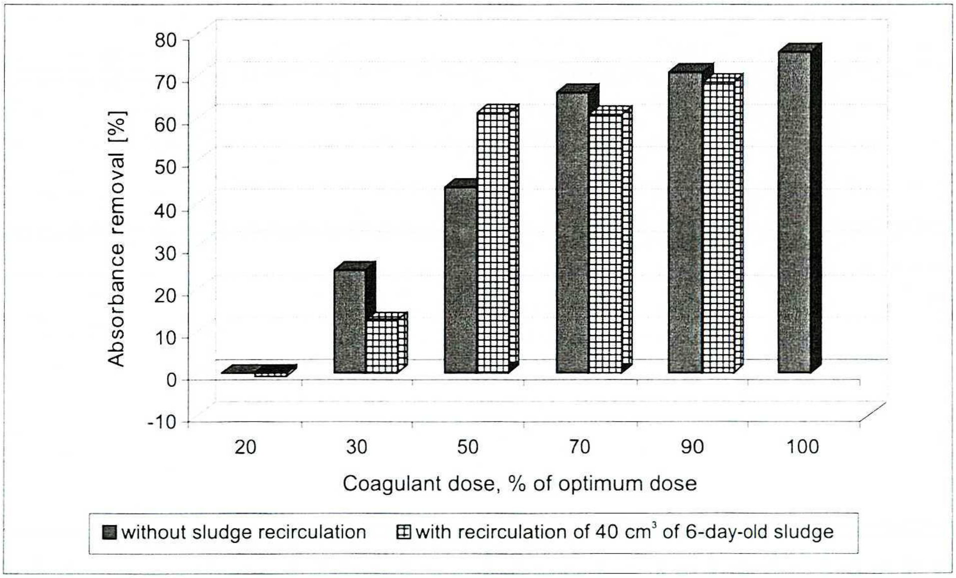

Fig. 7. Effectiveness of coagulation with recirculation of 40 cm^3 6-day-old sludge (absorbance removal)

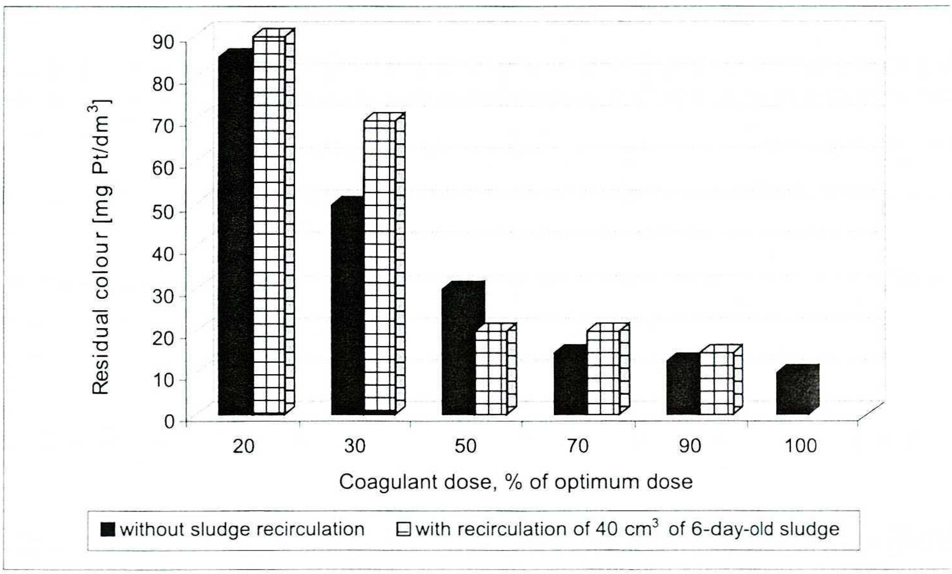

Fig. 8. Effectiveness of coagulation with recirculation of 40 cm^3 6-day-old sludge (residual color)

of turbidity and hence absorbance higher values. For 6-day sludge at the lowest alum doses residual color after treatment with sludge recirculation was higher in comparison to conventional treatment. So that, to make treatment with sludge addition possible, higher coagulant doses than in series with fresh sludge had to be applied, basing the process on sweep coagulation rather than electrostatic coagulation and charge neutralization. It was necessary to increase a dose to 50% of the optimum one. Higher doses (70%, 90%) had no significant influence on treatment operation with sludge recirculation and differences of absorbance values result from the fact that absorbance UV measurement depends not only on DOC concentration in water, but suspended solids, as well. For example, when coagulation without sludge was carried out at 70% of the optimum alum dose, 66.2% absorbance removal and residual color of 15 mg Pt/dm^3 were observed. For samples with sludge addition 61.2 % and 20 mg Pt/dm^3 values respectively were noted. Absorbance measurements in filtered samples, besides the lowest alum doses, indicate that floc ageing caused a little deterioration of sorption abilities, so the problem was agglomeration. The difficulty may be explained by the changes in sludge structure (lower dimension and higher density), which makes agglomeration more difficult.

On the basis of the comparative analysis of coagulation with sludge recirculation for 1-day and 6-day-old sludge the most distinct were differences of treatment effectiveness at 50% of the optimum alum dose. It may be concluded that this dose is a limiting value above which the sweep coagulation is dominating mechanism. This type of coagulation is needed to gain the proper agglomeration and clarification.

CONCLUSIONS

1. Sludge recirculation significantly enhances coagulation. When fresh post-coagulation sludge is recycled treatment effectiveness is much better in comparison to conventional coagulation.
2. When coagulation is conducted with fresh sludge recirculation much lower alum doses may be applied. The alum dose depends on the degree of sludge recirculation.
3. The influence of sludge recirculation on coagulation effectiveness depends on sludge age. Yet, 1-day sludge makes it impossible to produce water of better quality than at the optimum coagulant dose in conventional coagulation. Extension of retention time of sludge in a recirculation system up to 6 days results not only in lack of any positive effects on treatment process; it may cause its significant deterioration.

REFERENCES

[1] Benschoten van J.E., J.K. Edzwald: *Chemical aspects of coagulation using aluminum salts, Coagulation of fulvic acids using alum and polyaluminum chloride*, Water Research, **24**, 1527–1535 (1990).

[2] Benschoten van J.E., J.K. Edzwald: *Chemical aspects of coagulation using aluminum salts, Hydrolytic reactions of alum and polyaluminum chloride*, Water Research, **24**, 1519–1526 (1990).

[3] Black A.P., J.E. Singley, G.P. Whittle, J.S. Maulding: *Stoichiometry of the coagulation of color-causing organic compounds with ferric sulfate*, JAWWA, 10, 1347–1366 (1963).

[4] Dempsey B.A., R.M. Ganho, C.R. O'Melia: *The coagulation of humic substances by means of aluminium salt*, JAWWA, 4, 141–150 (1984).

[5] Duan J., J. Gregory: *Coagulation by hydrolyzing metal salts*, Advances in Colloid and Interface Science, 100-102, 475–502 (2003).

[6] Edzwald J.K.: *Coagulation in drinking water treatment: particles, organics, and coagulants*, Water Science Technology, 11, 21–35 (1993).

[7] Edwards G.A., A. Amirtharajah: *Removing color caused by humic acids*, JAWWA, 5, 50–57 (1985).

[8] Edzwald J.K., J.E. Tobiason: *Enhanced coagulation: US requirements and a broader view*, Water Science Technology, **40**(9), 63–70 (1999).

[9] Farmerie J.E.: *Clarification technologies*, [in:] XIX-th National, VII-th International Scientific and Technical Conference: Water Supply and Water Quality, Poland, Zakopane 2006.

[10] François R., A. van Haute, G. Winderick: *The influence of kinetic process parameters on flocculation characteristics*, [in:] The Practical Theory of Flocculation Processes, K.U. Leuven 1981.
[11] Gumińska J., M. Kłos: *Wpływ recyrkulacji osadu pokoagulacyjnego na skuteczność oczyszczania wody o dużej intensywności barwy*, Ochrona Środowiska, **30**, 1, 9–12 (2008)
[12] Hall E., R. Packham: *Coagulation of organic color with hydrolyzing coagulants*, JAWWA, 8, 1149–1165 (1965).
[13] Kim S-H., B-H. Moon, H-I. Lee: *Effects of pH and dosage on pollutant removal and floc structure during coagulation*, Microchemical Journal, **68**, 197–203 (2001).
[14] Narkis N., M. Rebhun: *Stochiometric relationship between humic and fulvic acids and flocculants*, Water Technology, 6, 325–328 (1977).
[15] Stumm W., J.J. Morgan: *Chemical aspects of coagulation*, JAWWA, 8, 971–992 (1962).

Received: April 22, 2008; accepted: November 22, 2008.

ROLA WIEKU OSADU RECYRKULOWANEGO W PROCESIE KOAGULACJI WÓD BARWNYCH

Celem stosowania urządzeń wielofunkcyjnych jest zwiększenie efektywności uzdatniania wody poprzez jednoczesne prowadzenie procesu flokulacji i sedymentacji. Cechą charakterystyczną tego typu urządzeń jest kontakt dopływającej wody z uprzednio wytworzonymi podczas flokulacji kłaczkami, umożliwiający pełne wykorzystanie ich właściwości sorpcyjnych. Z doświadczeń autorów wynika, iż dotychczas pomimo zasadniczych różnic w sposobie realizacji procesu uzdatniania pomiędzy układem konwencjonalnym, a układem, w którym zastosowano urządzenie wielofunkcyjne, dawka optymalna koagulantu dla obu układów jest ustalana według tej samej metodyki tzn. w oparciu o tzw. testy zlewkowe. W przypadku urządzeń wielofunkcyjnych metoda ta jest wysoce zawodna i często prowadzi do znacznego przedawkowania reagenta. W prezentowanej pracy przedstawiono wyniki badań nad rolą wieku osadu recyrkulowanego podczas koagulacji wód, których podstawowym zanieczyszczeniem są barwne związki organiczne. Na podstawie przeprowadzonych badań stwierdzono, iż możliwe jest obniżenie dawki optymalnej koagulantu w stosunku do dawki stosowanej w układzie koagulacji konwencjonalnej, jednak o skuteczności takiego rozwiązania decyduje zarówno stopień recyrkulacji osadu, jak również wiek osadu recyrkulowanego.