Comparison of traditional aluminum and ferric-based coagulants with zirconium-based coagulant. Evaluation of zirconium-based coagulants

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Abstract

Currently, there is no doubt of needing to develop and improve the treatment processes. Nowadays, increasingly used methods of water purification with the help of reagents, such as coagulation and flocculation. So there is need for improvement and finding more effective chemicals (EDZWALD & TOBIASON, 1999). An important role are playing environmental, natural and economic factors (P Jarvis, Jefferson, Gregory, & Parsons, 2005). The purpose of these studies is to compare the quality of water treatment of zirconium-based coagulants with traditional coagulants based on aluminum and iron. For achieving this goal, setting minimum dose of coagulants and working conditions for the occurrence of effective coagulation, coagulant doses studied depending on the residual turbidity and purities of suspended solids, phosphates and orthophosphate (Sharp, Jarvis, Parsons, & Jefferson, 2006). Data collected during the "Jar-test-experiments" and further analysis of selected water samples after coagulation. After carrying out the experiment on a model water in the laboratory, coagulants were tested in real conditions on the water treatment plant. Based on the results obtained by experiment, it was found that the minimum dose of the coagulants ZrNo, AlS, PIX-318 and ZrUkr are 3.3 mg / l, 3.4 mg / l, 3.5 mg / l and 4.4 mg, respectively. In this study results for the model solution are close to those obtained on the real waste water. That's why it indicates the correct choosing the dosing of coagulants and performance not only in laboratory conditions, but also in the production.

Keywords: water, treatment, coagulation, aluminium, ferrum, zirconium, phosphate removal

Introduction

Water treatment with chemicals is one of the most effective methods of water purification (Faust & Aly, 1998). Although many chemicals, namely coagulants available in the wastewater treatment, the rate of industrial development, climate change and economic problems forced to develop the traditional method. Common coagulants based on aluminum and iron, have several disadvantages such as residual aluminum (XIAO, ZHANG, & LEE, 2008) and reduce the quality of treatment water at a low pH of coagulants based on aluminum and iron, respectively (Duan & Gregory, 2003). The aim of this work is to evaluate the use of zirconium-based coagulants with traditional coagulants based on aluminum and iron. The report describes the degree of purification of water using conventional coagulants and compare them with the newer ones. Application of the proposed chemicals based on zirconium should simplify conditions of the coagulation process. It should extend the range of different degrees of purification of water pollution, making the process more economical (Peter Jarvis et al., 2012).

Materials and methods

Model water, was used in this research, hard and contained middle content of suspended particles (Engelbrecht & Mckinney, 2014). Its initial turbidity was approximately 300.0 nephelometric turbidity units (NTU) (Meozzi, n.d.). Its other properties were as follows:

pH=8.3; T-SS=120 mg/l; T-P=12.6 mg/l; OP=5.8 mg/l. The coagulants under investigation were an aluminum sulphate (AlS, Kemira), polyaluminium chloride (PAX XL-61), ferric sulphate (PIX-318, Kemira), and zirconium oxychloride based coagulants (ZrNo, Norwegian; ZrUk, Ukrainian).

The Zr coagulant contained 27% and 42% weight equivalent ZrO_2 respectively. Coagulants had specific gravity at 1.24 (ZrNo) and 1.38 (ZrUk) mg/l and a pH of <1 for both (Table 1).

Table 1 Coagulants properties

	Zr+4		**Al+3**		**Fe+3**
	ZrUk	ZrNo	AlS	PAX XL 61	PIX Xl-61
Ion, g/l	8.4	6.6	4.3	5.4	11.6
M, g/mol	322.2	322.2	342.2	342.2	815.55
density, g/cm3	1.38	1.24	1.3	1.27	1.50
pH	<1	<1	>2	>2,5	<1

After validation of the coagulant performance in laboratory jar tests, further experiments were carried out on real wastewater on NRV (Lillestøm).

Jar tests

Coagulation trials were undertaken on a Floculator 2000 jar tester using 6 cylindrical jars containing 1 L of raw water. Coagulation is performed in three steps of mixing: a rapid (60 sec, 400 rpm), the slow (10 min, 30 rpm), mixing and settling (30 min.) Using an automatic pipette, after the start phase of rapid stirring was added a coagulant, as well as during slow stirring, pH was measured. Water samples were analyzed for turbidity ("2100Q Portable Turbidimeter - Hach ®," nd), particulate matter (filtration, glass fiber filters), total phosphate and orthophosphate, which was carried out after filtration through 0.45 mm glass microfibre filter (Fisher Scientific, Loughborough , UK). This method for the determination of phosphate and orthophosphate based on spectrometric measurements of molybdenum complex with a further reduction of its ascorbic acid (ISO 6878:2004 "Water quality. & Method", 2004).

Jar-test on real wastewater includes all the steps that have been mentioned above. Except for the measurement of total phosphate and orthophosphate, which were carried out using the technology Lange Hach. Hach Lange is based on the method of formation of the molybdenum complex and ascorbic acid, but it is faster and easier to use.

Results and discussions

During the research work was conducted to compare the efficacy of purification the model and real wastewater using conventional coagulants based on aluminum and iron (AlS, PAX-Xl-61, PIX-318), and evaluation of zirconium-coagulants (ZrNo, ZrUkr).

One of the most important conditions for the effective conduct of the coagulation process is to determine the optimal doses of coagulants. The experiment was tested a dose range from 0 to 12 mmol / l of coagulant. Data obtained are reported in Figure 1.

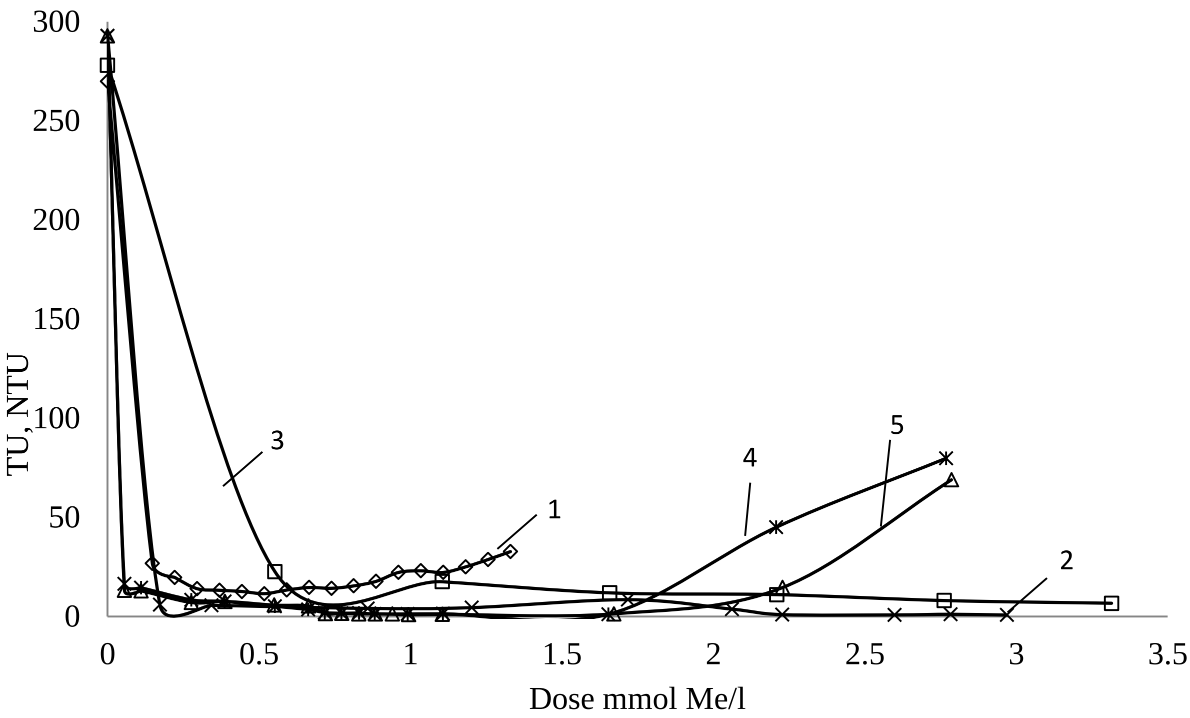

Figure 1 Dependence of turbidity on coagulant dose, 1 – AlS; 2 – PAX; 3 – PIX; 4 – ZrNo; 5 – ZrUk

The results of determining the optimal doses showed a dramatic reduction in haze from 300 NTU till about 5 NTU, at doses of 0.06 mmol Me / l for zirconium-coagulants and to 0.15, 0.5 mmol Me / l for aluminum and iron coagulants. So was defined interval doses of coagulants in which is a high degree of purification model water from the suspensions, causing blurred (up to 97% for the PAX Xl-61). Since zirconium coagulants have a wide range of doses compared with conventional coagulant, it can be used for application in relation to different degrees of water contamination.

The selected dose range for further purification model wastewater from suspended particles is purifying water of about 95% with the help of AlS and PAX XL 61.

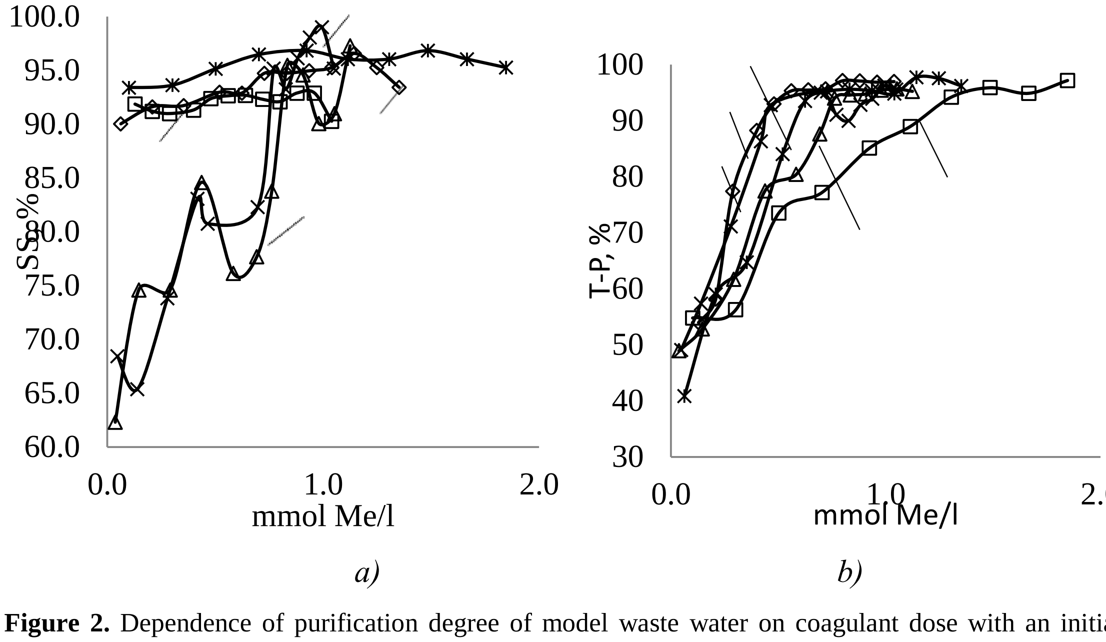

Figure 2. Dependence of purification degree of model waste water on coagulant dose with an initial dose of coagulant pH = 8 a - suspended solids; b - the total phosphate; 1 – AlS; 2 – PAX; 3 – PIX; 4 – ZrNo; 5 – ZrUk

Based on the above data, the working range of doses within 0.06-1 mmol Me / l coagulant is acceptable, since the degree of purification of phosphate and orthophosphate is an average of 60-85%, which is sufficient at this stage of water treatment.

As can be seen from the graphs, PAX XL-61skhozh AlS with the properties of aluminum sulfate has a greater degree of purification under these conditions. Thus for comparison, it suffices to use conventional coagulants based on aluminum and iron (ALS PIX-318).

Selection the conditions of coagulation process were conducted studies of influence doses of coagulants with the given initial pH of the model water (pH = 6-9.5) on the final coagulation pH.

Based on the experimental data revealed that necessary degree of purification is achieved in a dosage range from 0.06-1 Me mmol / l, which were further explored.

Selecting the range of pH values determined by the fact that the maximum intensity of the biological purification process is achieved at pH 7.0 - 8.2, while at pH below 6.0 and above 9.5 is completely inhibited.

Zirconium-based coagulant lowers the pH less than aluminum and iron coagulants. Reduction of pH by using an aluminum and iron-based coagulant and ranges from 1 to 1.5 units. given initial pH 9.5-6, which further needs more reagents to maintain working pH. This behavior can be due to various chemical properties of selected coagulants:

$$ZrOCl_2 \cdot 8H_2O \rightarrow ZrO(OH)_2\downarrow + 2Cl^- + 2H^+ + 6H_2O \quad (1)$$

$$Al_2(SO_4)_3 \cdot 18H_2O \rightarrow 2Al(OH)_3\downarrow + 3SO_4^{2-} + 6H^+ + 12H_2O \quad (2)$$

$$FeCl_3 \cdot 6H_2O \rightarrow Fe(OH)_3\downarrow + 3Cl + 3H^+ + 6H_2O \quad (3)$$

$$Fe_2(SO_4)_3 \cdot 9H_2O \rightarrow 2Fe(OH)_3\downarrow + 3SO_4^{2--} + 6H^+ + 3H_2O \quad (4)$$

According to the chemical reactions (1.4), result is the formation of 1 mole of zirconium hydroxide which forms two moles of acid. While in the hydrolysis of aluminum and iron coagulants form 3-6 moles of acid. Thus, needs a greater amount of alkali to neutralize the acid and maintain the operating pH .

On the basis of pH studies were selected operating conditions of the coagulation process, t = 20 ° C, pH = 6-8. These values correspond to the desired pH for economic efficiency, speed of reaction and efficiency of water purification. By the fact that nucleation occurs slowly at lower pH and leads to the formation of a colloidal solution. Thus it reduces the effectiveness of water purification. Also, with increasing pH, the instantaneous solution satiety accrues. Thus it leads to rapid deposition and maturation of the sediment, which has negative affect on the efficiency of purification.

Under selected conditions (pH and T) of the coagulation process, were investigated the effect of pH of the model water on purification affiance from suspended solids, residual turbidity, total phosphate and orthophosphate.

Coagulants purification efficiency from suspended particles is 80-90% when using aluminum- and iron-based coagulants. While zirconium-based shows only 55-80% at the selected operating range of coagulant doses. Further studies were carried out on the residual turbidity of the water in the model.

Residual turbidity of zirconium-based coagulants is 14-16 NTU, at concentrations of coagulant 0.04-0.05 mmol Me/ l. While the residual turbidity of aluminum and iron coagulant is 20 cm / l under these conditions. This indicates a more efficient purification of the turbidity on model water, using zirconium at pH = 7, 6 and the initial pH = 8. Thus the ability of zirconium-based coagulants to purify colloids more efficient then aluminum and iron coagulants. Because of specific structure of the colloidal particles of hydrated zirconium oxide, which has a charge of 4 + ion, unpaired ions that contributes adsorption .

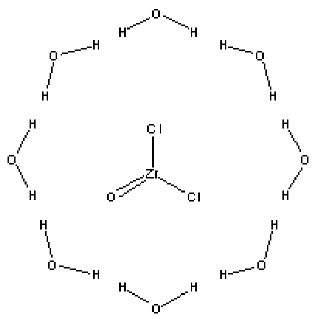

Figure 3 Structure of zirconium oxychloride $ZrOCl_2*8H_2O$.

and 8, respectively, the to its greater capacity of

Besides, one of the important parameters of water treatment is the purification of the total amount of phosphates and orthophosphates. To determine the purification efficiency of phosphates, have been carried several experiments using the above coagulants under specified conditions (Figure 4).

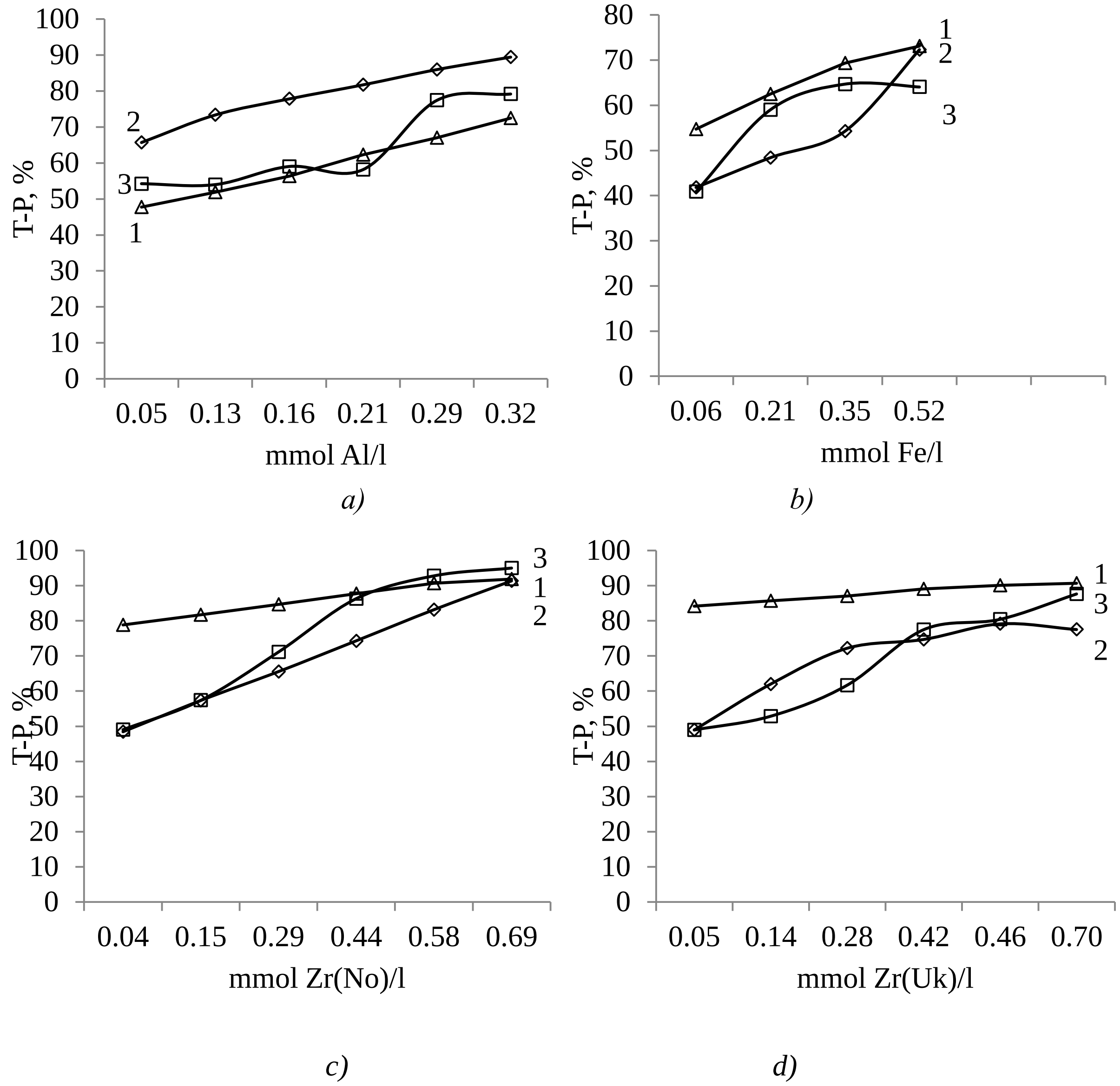

Figure 4 Purification efficiency phosphates on coagulant dose: *а* – AlS; *б* – PIX; *в* – ZrNo; *г* – ZrUk; 1 – pH=6,0; 2 – pH=7,3; 3 – pH=8,0

During purification process, metal partly goes both on removing suspended substances and phosphates. Most of the aluminum and iron precipitate suspended solids. But the purification efficiency of the total PO42- on average is only 55% (Figure 4. a, b). While, the value of T-P for zirconium coagulant is 80-85% under the same conditions (Figure 4. c, d). This behavior is explained by the formation of an insoluble precipitate zirconium phosphate:

$$Zr^{+4} + H_3PO_4 = Zr_3\,(PO_4)_4 + nH^{+} \qquad (5)$$

Due to this reaction, a precipitation formed $Zr_3(PO_4)^{4}$. So the product has much higher solubility (Pr = 1 * 10-132) than iron and aluminum salts (Pr = 1.3 * 5.75 * 10-22 and 10-19, respectively). Thus, even at low concentrations of zirconium-reagent, occurs almost complete precipitation of phosphate.

Also, were conducted extra studies, to determine coagulants ability to purify water from orthophosphate.

From the above data, the zirconium-based coagulants have a purification efficiency of orthophosphate like phosphates. Thus, it indicates the efficient purification of organic and inorganic impurities of phosphate in the water. The exception is the iron-coagulant, which according to the literature (Kul LA, nd) most reacts with organic substances in the water. Thus causing the difference between the readings of the T-P and PR.

Based on the data which were obtained in the laboratory, coagulants were tested on a real waste water on NRA in Lillestrom.

Further data of removing suspended solids, phosphates and orthophosphate are shown in Figure 5.

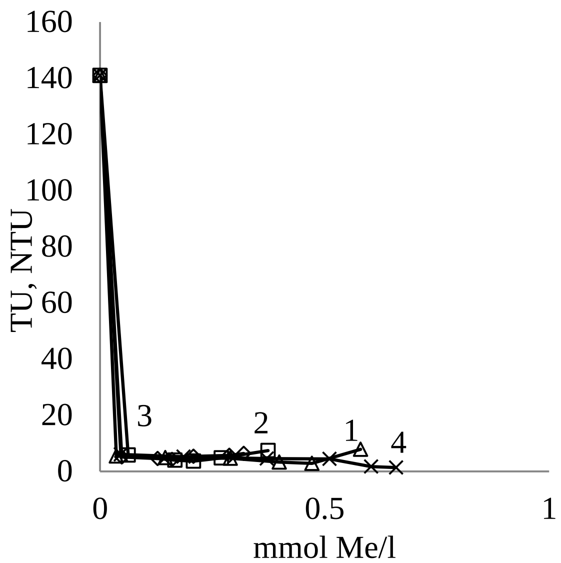

Figure 5 Purification efficiency from turbidity of coagulant dose at the initial value. pH=6,5: *a* –: 1 – AlS; 2 – PIX; 3 – ZrNo; 4 – ZrUk

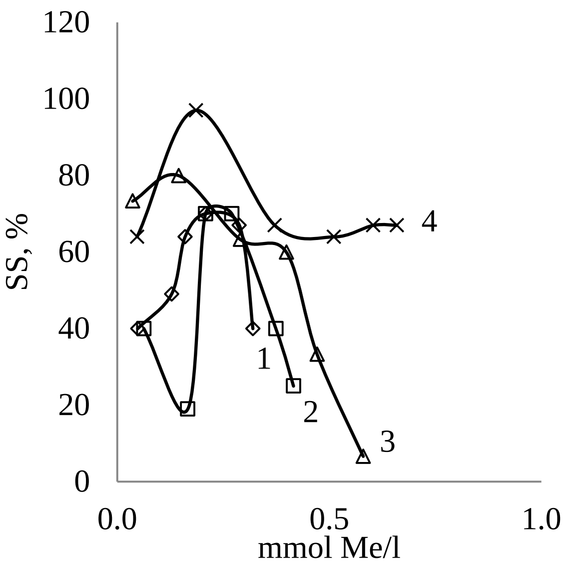

Figure 6 Purification efficiency from suspended solids of coagulant dose at the initial value. pH=6,5: 1 – AlS; 2 – PIX; 3 – ZrNo; 4 – ZrUk

Based on the figure, minimal doses of coagulants, which were selected in the laboratory are suitable for cleaning real wastewater. Each coagulant has minimal residual turbidity after coagulation about 5.5 NTU, at doses of coagulants at 0.04 mmol / l, 00.05 mmol / l, 0.05 mmol/ l and 0.07 mmol / l respectively for ZrNo, ZrUkr, AlS, and PIX-318. Thus, ZrUkr has the largest purification rate of suspended solids at 97%, at dose of 0.18 mmol/l. However, in industrial conditions enough purification efficiency lies in the range 70-80%, which is achieved by addition of 0.04; 0.05; 0.16 and 0.21 mmol Me/l for ZrNo, ZrUkr PIX-318 and AlS respectively.

During the experiment, the degree of wastewater purification from phosphates and orthophosphates was determined on the real water on the wastewater plant in the city Lillestrom. The experimental data are presented in Figures 7 and 8.

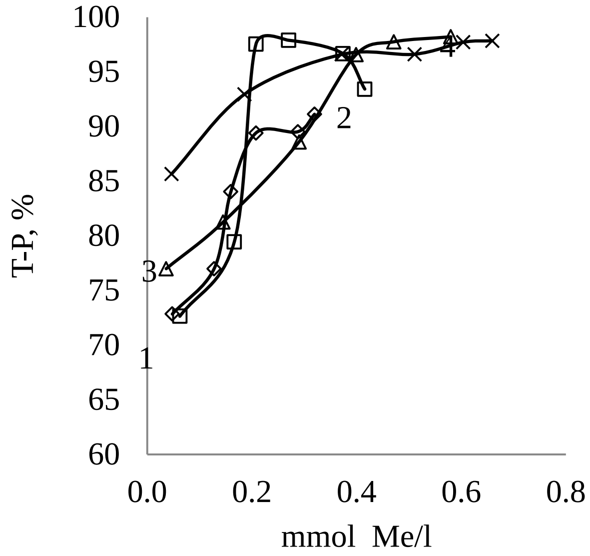

Figure 7 Purification efficiency from total phosphates of coagulant dose at the initial value. pH=6,5:: 1 – AlS; 2 – PIX; 3 – ZrNo; 4 – ZrUk

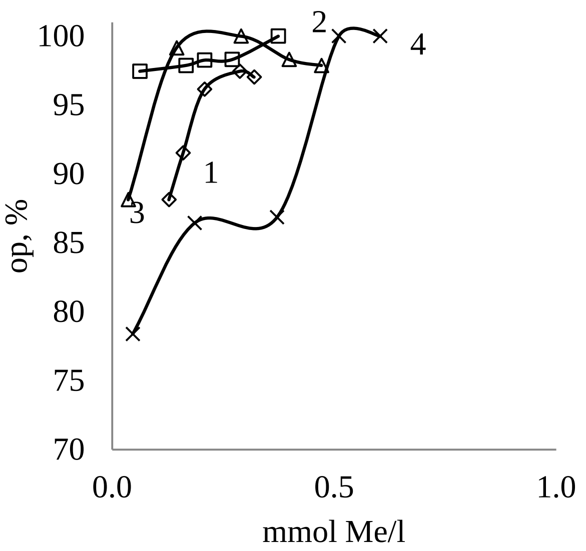

Figure 8 Purification efficiency from orthophosphates of coagulant dose at the initial value. pH=6,5:: 1 – AlS; 2 – PIX; 3 – ZrNo; 4 – ZrUk

Biological treatment is next step in water treatment process which occur in presence of microorganisms, requiring as a nutrient medium phosphorus-containing compounds. Thus, there is no need for a complete removal of phosphorus-containing impurities. The required purification efficiency of waste water from phosphates and orthophosphates achieved at a dose of zirconium-based coagulant 0.04 mmol Zr/ l and amounts to 75-85%.

Conclusion

During this research work were analyzed and compared two traditional coagulants (based on aluminum and iron), and two zirconium-based coagulant. Under laboratory conditions were determined conditions for quality of the process of coagulation, which according to experimental data is coagulation pH = 6 ... 8. Also, were defined minimal doses of coagulants at 0.04 mmol / l, 0.05 mmol / l, 0.05 mmol / L and 0.07 mmol / L, for ZrNo, ZrUkr, AlS and PIX-318, respectively. Coagulants were tested for the ability purify to model and wastewater from suspended solids, total phosphate and orthophosphate. Zirconium-based coagulants have purification efficiency from phosphate about 75-85%. at doses of 0.04-0.05 mol Zr / l, which is more effective as compared to traditional coagulants. The study has confirmed the effectiveness of water purification both in the laboratory on a model solution and in the factory, on the real wastewater.

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