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ON THE CONTRIBUTION OF PHYSICOCHEMICAL PROCESSES TO THE COAGULATION OF SURFACE WATER POLLUTANTS WITH ALUMINIUM-BASED OR IRON(III)-BASED COAGULANTS

Coagulation with aluminium- or iron-based flocculants is paralleled by direct reactions with humic substances bringing about a high efficiency of destabilisation and, consequently, a high efficiency of organic matter removal. The coagulation process also involves competitive reactions concomitant with the hydrolysis of the coagulant, which induce the formation of positively charged complexes. The efficiency of organic matter removal via competitive reactions is much lower, as the destabilisation of the colloids proceeds in an indirect way.

The contribution of the two reaction groups depends on the value of the Ca/Mg molar ratio. The adverse effects produced by competitive reactions can be eliminated or reduced by selective dosage of inert calcium salts (e.g. CaCl₂) or magnesium salts (e.g. MgSO₄). Selective dosage of both coagulants, i.e. aluminium and iron, may also be advantageous. The application of a high gradient ($G > 300 \text{ s}^{-1}$) during rapid mixing along with an optimum coagulant dose also diminishes some of the disadvantageous phenomena involved.

1. INTRODUCTION

One of the major factors that affect coagulation process is the presence of humic substances in the water to be treated [1], [2]. An inherent advantage of humic substances is their ability to bind cations, including those of calcium and magnesium. The input energy for a humus complex, e.g. for humic acids, is described by the following sequence [3]:

$$\text{H} > \text{Pb}, \text{Cu}, \text{Fe}^{3+} > \text{Zn} > \text{Fe}^{2+} > \text{Ni} > \text{Co} > \text{Mn} > \text{Mg} > \text{Ca} > \text{Ba}, \quad (1)$$

whereas the output energy is characterised by the same sequence in the opposite direction.

The humic substances, which occurred in the riverine water samples being investigated (coming from the Odra river and its tributary, the Oława river), showed a greater affinity for magnesium than for calcium cations. Thus, following treatment with an inert calcium salt (CaCl₂) and an inert magnesium salt (MgSO₄), the humic

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substances in the same water samples were able to bind 1.3 times (the Odra river water) and 1.9 times (the Oława river water) as many magnesium cations as calcium cations [4]. The physicochemical properties of the humic substances that affect coagulation depend on their micellar structure [5] (figure 1). Thus, mainly calcium and magnesium cations (and occasionally aluminium cations and aluminium hydrolysis products) are bound by the carboxyl groups on the surface of the humic substance molecules (SH). The cations mentioned (including monovalent cations, e.g. those of sodium) are also bound in the diffuse part (D).

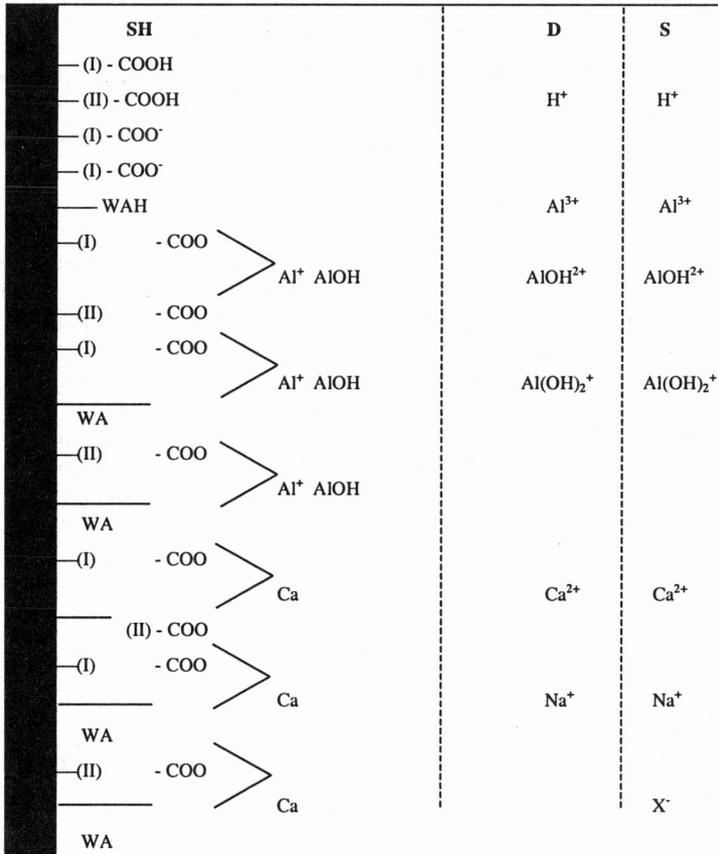


Fig. 1. Double-layer model of humic substances [5]

The diffuse part (D) is in contact with the bulk solution (S), where cations dominate (in the immediate vicinity of the diffuse part) and anions are less frequent. The quantity of the cations bound in the mentioned parts depends on pH, which strongly affects the degree of dissociation of carboxyl and phenolic groups. According to Don-

nan's membrane equilibrium concept, two conditions must be fulfilled: that of the equality of the chemical potential of the electrolyte in the solution and in the diffuse part, and that of electroneutrality at each point of the system. Hence, the concentration of cations in individual parts can be written as

$$\frac{[H^+]_D}{[H^+]_S} = \frac{[M^+]_D}{[M^+]_S} = \left(\frac{[M^{2+}]_D}{[M^{2+}]_S} \right)^{1/2} = \left(\frac{[M^{3+}]_D}{[M^{3+}]_S} \right)^{1/3} \quad (2)$$

From these relations it can be inferred that each change of cation concentration in the solution is concomitant with a change in the diffuse part (D).

Another factor affecting the coagulation process is the Ca/Mg molar ratio in the water [1], [2]. Sequence (1) as well as the results obtained with the Odra and the Oława water samples show that magnesium has a greater affinity for the humus complex, and therefore, in sequence (1), magnesium is on the left-hand side with respect to calcium. However, it is a well-established fact that the input energy can be varied by increasing the concentration of one of the cations (as in the ion-exchange process). In order to expel the left-hand-side cation from the ion exchanger, it is necessary that the concentration of the cations is twice or three times as high as the concentration of the ion being exchanged [6]. Hence, the value of the Ca/Mg ratio exerts an influence on the cation exchange processes during coagulation.

Coagulation process is additionally affected by the electrical state of the interfacial surface, and particularly by the ζ -potential and the net total particle surface charge density δ_p , which can be described by the following equation [7]:

$$\delta_p = \left(\frac{C_T}{K_{1C}[H^+] + K_{2C}[Ca^{2+}] + 1} \right) (K_{2C}[Ca^{2+}] - 1), \quad (3)$$

where C_T denotes total adsorption concentration, K_{1C} indicates the dissociation constant of functional groups of humic complex (carboxyl and phenolic groups), and K_{2C} is the instability constant of the complex of humic substances and Ca^{2+} or Mg^{2+} .

The equation shows that the net particle charge depends on the humic substance content, pH and calcium or magnesium concentration in the water under treatment.

2. METHODS

The laboratory experiments were carried out with highly polluted (the Odra, 263 km from the source) and less polluted (the Oława, 1 km from the confluence with the Odra) riverine water samples. A jar test apparatus (Phipps and Bird) equipped with

2 dm³ jars was used (1 min of rapid mixing, 15 min of slow mixing and 30 min of settling). The samples were treated with calcium chloride (10 and 20 g of Ca²⁺ per m³) or magnesium sulphate (6 and 12 g of Mg²⁺ per m³) approximately 8 minutes before the coagulant was dosed. The coagulant doses applied were varied (30, 60, 100 g of Al(SO₄)₃ · 18H₂O/m³) or constant (100 g of Al(SO₄)₃ · 18H₂O/m³ and 47 g of Fe(III) chloride). For comparison, coagulation was carried out without addition of calcium or magnesium salt in order to determine the effect of both species on the composition of the water. To establish the influence of the velocity gradient during rapid mixing on the efficiency of coagulation, the values of the gradient were varied in the range from 58 s⁻¹ to 465 s⁻¹. After the coagulation process had been terminated, the samples were filtered through a filter paper and analysed for physicochemical composition.

The riverine water samples showed similar concentrations of organic pollutants. The concentration of humic acids ranged from 2 to 7 g/m³, whereas colour intensity varied between 15 and 80 g/m³. The hardness and alkalinity of the Oława water samples were by about 80% higher than those of the Odra.

3. PHYSICOCHEMICAL PHENOMENA CONCOMITANT WITH COAGULATION

Coagulation doses induce two competitive processes:

- direct reactions of the coagulant, or hydrolysis products, with humic substances,
- reactions of the coagulant with hydrogen carbonates; as a result hydrolysis reactions are initiated.

The reactions of humic substances with the coagulants depend on the type of the coagulant and the value of the Ca/Mg ratio. These are ionic reactions because, as a result, calcium is exchanged for magnesium or magnesium is exchanged for calcium (according to the Ca/Mg ratio), or there is only calcium loss or magnesium loss (figure 2). The yield of the reaction also depends on the value of the Ca/Mg ratio. For extreme values of the Ca/Mg ratio, the yield of the reaction, e.g. in the Odra river water samples, was maximal, and so was the yield of the reaction with humic substances, which provided the highest removal efficiency of organic pollutants (figure 3). This is so because the reactions run at a fast rate in the entire volume of the solution. As the Ca/Mg ratio tends to the equilibrium value, the yield of the direct reactions of humic substances with the coagulant decreases, and so does the efficiency of organic matter removal (figure 3). The yield of the reaction takes a minimum value at a Ca/Mg ratio at which the replacement of calcium by magnesium or magnesium by calcium is the poorest. Such state can be regarded as the state of calcium–magnesium equilibrium in the complex. For the Odra river water such equilibrium state was obtained at the Ca/Mg ratio of 2 to 3; for the Oława water samples, at the Ca/Mg ratio higher than 3.5 [4].

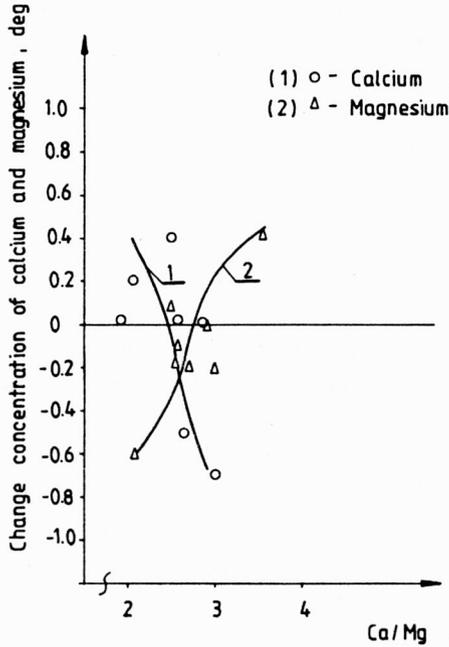


Fig. 2. Variations in calcium and magnesium concentrations following coagulation of the Odra river water by alum versus Ca/Mg molar ratio ($D_{Al_2(SO_4)_3 \cdot 18 H_2O} = 100 \text{ g/m}^3$)

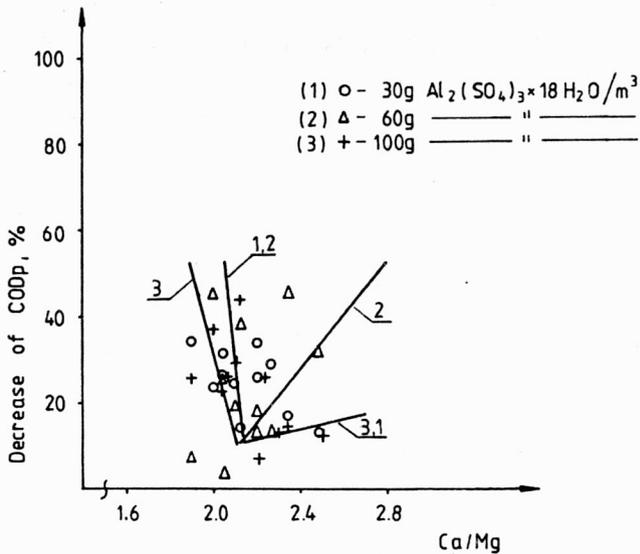


Fig. 3. Efficiency of COD_p removal following coagulation of the Odra river water by alum versus coagulant dose and Ca/Mg molar ratio

The said equilibrium state enhances the reaction of the coagulant with bicarbonates, and this accounts for the decrease in the efficiency of organic matter removal. In other words, the utilisation of the coagulant in direct destabilisation of humic substances is poorer. The role of the reaction of the coagulant with hydrogen carbonates increases with the increasing alkalinity of the water, as there is a concomitant rise in the rate of their hydrolysis.

4. ION-EXCHANGE PROCESSES DURING COAGULATION

The exchange of magnesium cations for calcium cations and vice versa during the coagulation is associated with the Donnan (membrane) equilibrium, with the energy necessary for cations to form the complex with humic substances (which determines the sequence of formation), and with the concentration effect (which is expressed in terms of the Ca/Mg ratio). If the Ca/Mg ratio falls below the equilibrium value, the coagulant, i.e. the Me^{3+} cations, as well as the hydrolysis products, $\text{Me}(\text{OH})^{2+}$ and $\text{Me}(\text{OH})_2^+$, which react with the humic substances, penetrate the diffuse part (D) of the complex according to the principle of cation concentration equalisation (2) and higher input energy. As a result, the cations of a lower input energy, i.e. Ca^{2+} cations, are displaced (1). The cations then penetrate the adsorption layer to be bound to the dissociated (mainly carboxylic) groups (water pH after coagulation of the investigated water samples was below 7). According to the Donnan principle, there occurs equalisation of concentrations in the diffuse part. This time – according to the input energy value – it is magnesium (Mg^{2+}) that enters the complex. Following termination of the coagulation process, there is a decrement of magnesium cations and an increment of calcium ions (figure 2). As the value of the Ca/Mg ratio increases, the affinity of the humic complex for magnesium cations decreases to reach the minimum value at the calcium–magnesium equilibrium point of the complex.

If the Ca/Mg ratio takes the values which are greater than the equilibrium value, the coagulant reacts with the humic substances, but the pattern is in some way different. At the first stage, magnesium cations are displaced by the diffuse part owing to the concentration effect produced by the excess of calcium cations; at the second stage, calcium cations enter the complex (figure 2). As a result, in the coagulation process there is a decrement of calcium cations and an increment of magnesium cations.

5. PHYSICO-CHEMICAL PHENOMENA IN IRON(III) CHLORIDE COAGULATION

When the Ca/Mg ratio takes extreme values, Fe^{3+} cations and hydrolysis products, i.e. $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$, react with humic substances. Also bicarbonate reactions yielding positively charged cations are likely to occur. Hence,

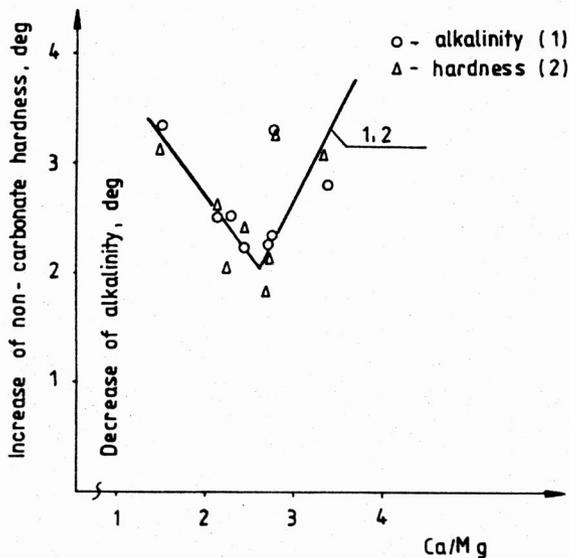


Fig. 4. Variations in alkalinity and non-carbonate hardness following coagulation of the Odra river water by Fe(III) chloride versus Ca/Mg molar ratio ($D_{FeCl_3} = 47 \text{ g/m}^3$)

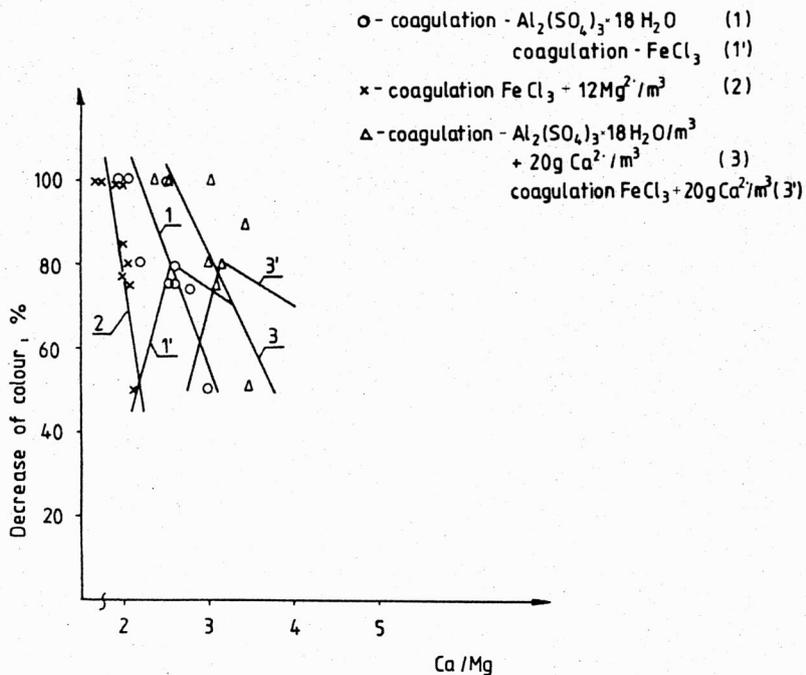
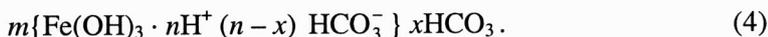
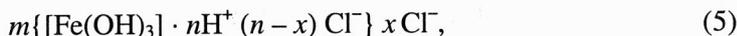


Fig. 5. Efficiency of coloured matter removal following coagulation of the Odra river water by alum or Fe(III) chloride



As the values of the Ca/Mg ratio approach those of the calcium–magnesium equilibrium, the reaction rate (and, consequently, the yield of the direct reaction of the coagulant with humic substances) decreases. The role of the reactions which produce systems like [8]



thus accounting for destabilisation (based on the principle of the oppositely charged colloid), is likely to become increasingly important. Such a course of the reaction has been corroborated by the results obtained when investigating the relationship between the decrement in alkalinity and the increment in non-carbonate hardness during coagulation of the Odra river water samples. The maximum decrement in alkalinity with a concomitant increment in non-carbonate hardness was found to occur at extreme values of the Ca/Mg ratio and the minimum one for both the factors (50 to 70% of calculated value) at the calcium–magnesium equilibrium of the complex (figure 4). Similar results were obtained using iron(II) sulphate oxidised with chlorine [9]. This indicates that the rate at which the Fe(III) cations react with humic substances is higher than the ratio of the hydrolysis reaction. The reaction of Fe^{3+} cations and hydrolysis products with humic substances also yields soluble coloured complexes, which is evidenced by the pattern of removal efficiency variations for humic substances and by the decrease of colour intensity which increases with the Ca/Mg ratio to reach the maximum value for the state of calcium–magnesium equilibrium in the complex, and the minimum value for the lowest Ca/Mg ratio (both for the Odra and for the Oława) (figure 5). Similar results were obtained using chlorine-oxidised Fe(II) sulphate as a coagulant [9].

6. PHYSICO-CHEMICAL PHENOMENA CONCOMITANT WITH ALUM COAGULATION

When the Ca/Mg ratio takes extreme values, humic substances come into reaction partly with the hydrolysis products $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$ and probably also with complexes of the following type:



When the value of the Ca/Mg ratio tends to the calcium–magnesium equilibrium of the complex owing to the decrease in the rate of the reaction with humic substances (and consequently in the yield), the efficiency of the reaction with hydrogen carbonates (and consequently the efficiency of hydrolysis) increases. At the point of the

calcium–magnesium equilibrium of the humus complex, destabilisation of the colloids follows the principle of the reaction with a colloid of an opposite sign:

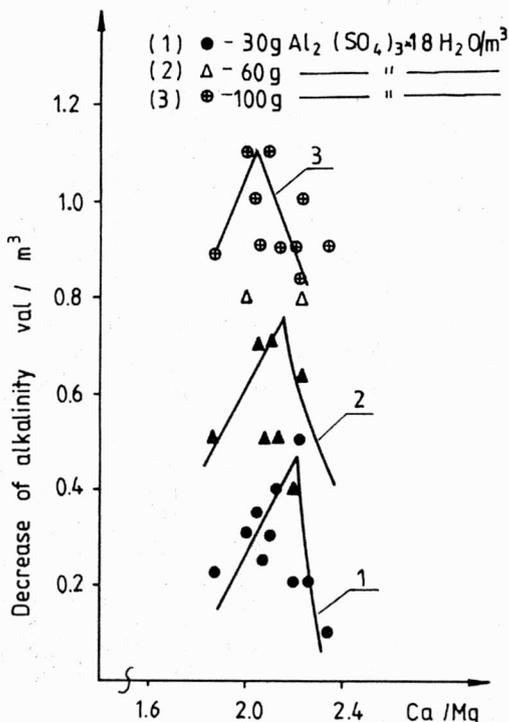
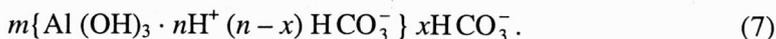


Fig. 6. Alkalinity variations following coagulation by alum versus coagulant dose and Ca/Mg molar ratio

Such a course of the reaction is evidenced by the changes in alkalinity decrement and in the concomitant increment of non-carbonate hardness. Maximal values occur at the point of the calcium–magnesium equilibrium of the complex and correspond with the calculated values, whereas minimal values appear when the Ca/Mg ratio takes extreme values (figure 6). And this indicates that the hydrolysis rate is faster for the aluminium coagulant than for the iron-based coagulant. Unlike the ferric coagulant, the reaction of the aluminium coagulant with humic substances yields sparingly soluble complexes, which manifests itself in the change of the removal efficiency for humic substances in the course of the coagulation process. Thus, coloured matter was removed with the maximum efficiency at the lowest value of the Ca/Mg ratio – both for the Odra and for the Olawa water samples (figure 5). It seems therefore advisable

to perform coagulation with two coagulants – an aluminium coagulant, e.g. aluminium sulphate, and an iron-based coagulant, e.g. Fe(III) chloride. The selection of appropriate coagulants depends on the value of the Ca/Mg ratio.

7. EFFECT OF WATER ALKALINITY ON THE COURSE OF THE COAGULATION PROCESS

The rate of hydrolysis, and consequently its efficiency after coagulation, depends on the alkalinity of the water to be treated. In waters of increased alkalinity, there is no substantial difference in the degree of alkalinity decrement, as it can be seen during coagulation of the Olawa river water with an aluminium- or iron-based coagulant (figures 7 and 8). This evidences that the rate of coagulant hydrolysis in the said riverine water is noticeably faster. The increased participation of the coagulant reactions with hydrogen carbonates deteriorates the conditions for direct reactions of the coagulant with humic substances, and this should be attributed to the decrease in the concentration of cations and in the amount of indirect hydrolysis products, such as

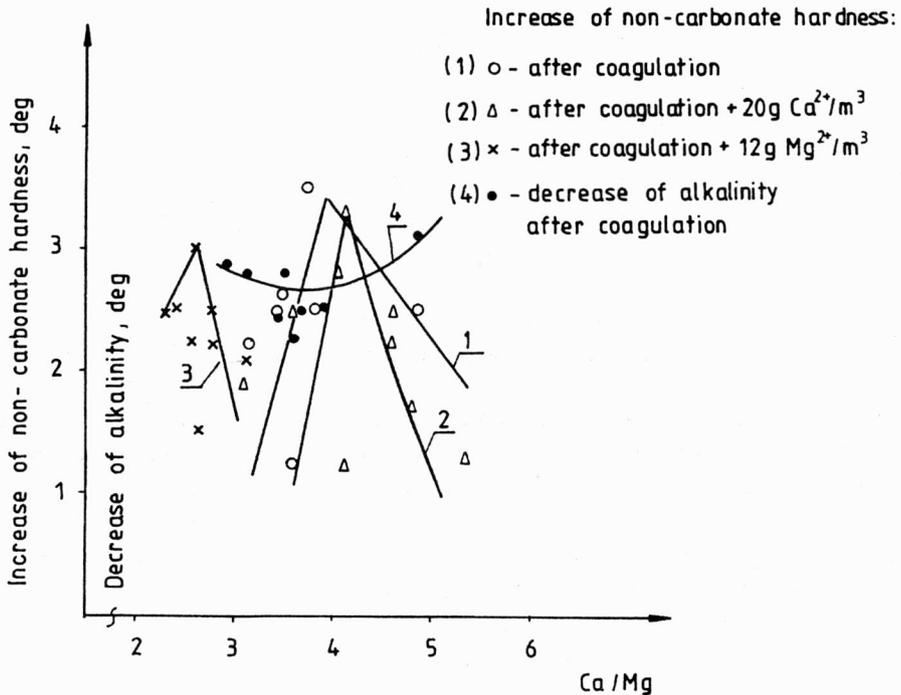


Fig. 7. Alkalinity and non-carbonate hardness variations following coagulation of the Olawa river water by alum versus Ca/Mg molar ratio ($D_{\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}} = 100 \text{ g/m}^3$)

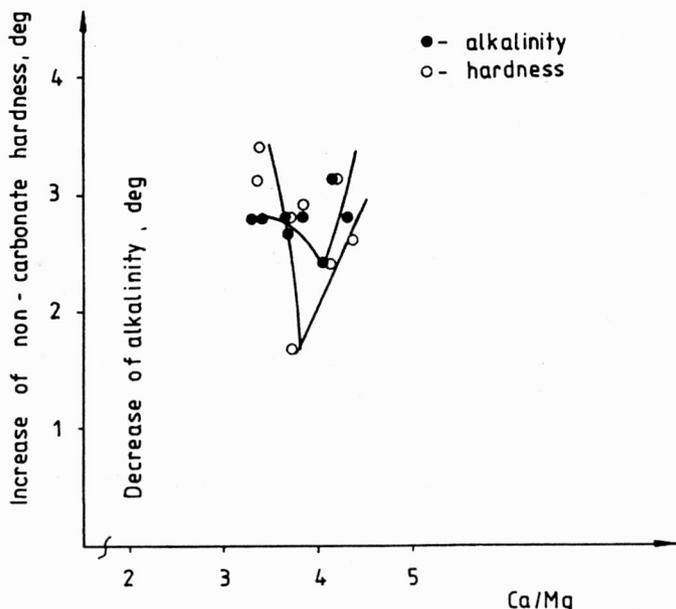


Fig. 8. Alkalinity and non-carbonate hardness variations following coagulation of the Olawa river water by Fe(III) chloride versus Ca/Mg molar ratio ($D_{\text{FeCl}_3} = 47 \text{ g/m}^3$)

$\text{Me}(\text{OH})_2^{2+}$, $\text{Me}(\text{OH})_2^+$ or Me^{3+} . As a result, the efficiency of organic matter removal from the Olawa river water decreases. This holds particularly for the iron-based coagulant, because there is a decrease in the concentration of such cations as Fe^{3+} , $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_2^{2+}$. The result is that the removal efficiency of organic pollutants falls considerably (averaging 10% for both coagulants). The contribution of the reactions, where oppositely charged colloids take part (equations (4) to (7)), begins to increase. This finding is corroborated by the variations in alkalinity and permanent hardness (figures 7 and 8). The phenomena mentioned reduce the utilisation of the coagulant, thus decreasing the efficiency of organic matter removal.

8. EFFECT OF NEUTRAL CALCIUM OR MAGNESIUM SALTS ON THE COURSE OF COAGULATION

Neutral calcium or magnesium salts change the conditions for the calcium–magnesium equilibrium of the complex which is penetrated by calcium or magnesium cations, thus contributing to the change in the density of the negative surface charge (equation (3)). In that particular case, this means a decrease, because the net particle charge – at an approximately constant pH – depends mainly on the fixation of the negative groups in the complex, primarily by calcium and magnesium cations.

The addition of calcium or magnesium salts also changed the Ca/Mg ratio in the water. The point of calcium–magnesium equilibrium in the complex is shifted towards the region where direct reactions of the coagulant with humic substances occur with a high yield. As a result, there occurred an inversion of the relationship between the efficiency of organic matter removal and the Ca/Mg ratio (figure 9). Such data were obtained for the Odra water samples for two concentrations of calcium chloride or magnesium sulphate [4], while for the Oława water samples, similar results were achieved solely for the aluminium coagulant, at a maximum dose of calcium chloride [4]. For the Oława river water being coagulated by Fe(III) chloride – at similar doses of calcium salts or magnesium salts – there was no inversions of the relationship between the efficiency of organic substance removal and the value of the Ca/Mg ratio. What is more, after addition of magnesium salts the efficiency of the coagulation process decreased [4].

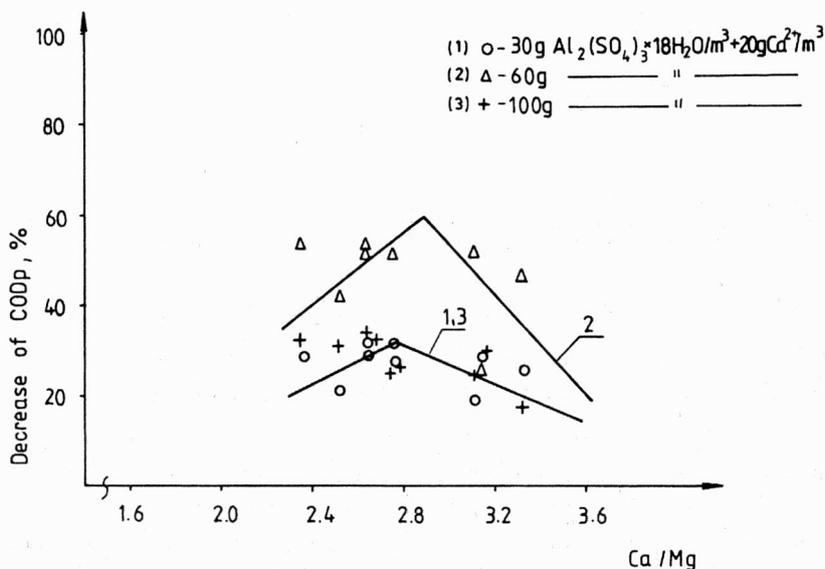


Fig. 9. Efficiency of COD_p removal following coagulation of the Odra river water, which contains calcium chloride, by alum versus coagulant dose and Ca/Mg molar ratio

This pattern should be attributed to the increased alkalinity on one hand and to the decreased density of the negative surface charge on the other hand, which is greater for magnesium salts because of the greater affinity of humic substances for these cations. Due to increased reactivity of the coagulant with respect to bicarbonates, there is a decrease in the concentrations of the Fe^{3+} cations and such hydrolysis products as $Fe(OH)_2$ and $Fe(OH)^{2+}$. Summing up, the weakening of the electrostatic interaction forces, which occurs at the same time, brings about a decrement in the yield of direct reaction with humic substances.

9. OPTIMUM COAGULANT DOSE

The determination of the optimum coagulant dose is of prime importance. Under defined physicochemical conditions, the optimum dose provides maximal removal efficiencies (including those for organic and humic substances) and optimises each process involved in coagulation.

Investigations of the alum coagulation of the Odra river water (with 30, 60 and 100 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}/\text{m}^3$ doses) showed that the optimum dose depended not only on the pollution level, but primarily on the Ca/Mg molar ratio. Thus, when the value of the Ca/Mg ratio was lower than that in the calcium–magnesium equilibrium in the humus complex, the optimum alum dose for the Odra river water amounted to 30 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}/\text{m}^3$; for the greater Ca/Mg ratios the optimum dose totalled 60 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}/\text{m}^3$ (figure 3). Further increase of the alum dose (100 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}/\text{m}^3$) deteriorated the efficiency of organic matter removal (figure 3). This adverse effect should be attributed to the reactions competitive with water alkalinity. Another unfavourable effect produced by the increased alum dose was the increase of hydrolysis rate, which reduced the participation of direct reactions of the dissociation and hydrolysis products with humic substances. It was found that the minimum efficiency of alum hydrolysis increased with the increasing alum dose. The minimum efficiencies of hydrolysis for 30, 60 and 100 g doses of $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}/\text{m}^3$ amounted to 40%, 62.5% and 81.8%, respectively, and were determined from the relationship between the alkalinity decrement and the Ca/Mg ratio and coagulant dose (figure 6). The maximum decrement of alkalinity (figure 6) corresponds with the approximately maximum efficiency of hydrolysis resulting from the alum dose applied (according to the reaction):



Minimum efficiency of hydrolysis was defined as the ratio of the minimum to the maximum decrement in alkalinity (figure 6) expressed in per cent for an appropriate coagulant dose.

When coagulation was carried out at the optimum coagulant dose, the efficiency of organic matter removal from the Odra river water samples varied considerably (from 10 to 45%; figure 3). When a neutral calcium salt (CaCl_2) was dosed in the quantity of 20 g $\text{Ca}^{2+}/\text{m}^3$ as a prior step, it was possible to invert the relationship between the efficiency of COD_p removal and the Ca/Mg ratio (figure 9). The efficiency of COD_p removal in the state approaching the calcium–magnesium equilibrium in the humus complex for the dose of 60 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}/\text{m}^3$ (which is the optimal one) amounted to 55% (figure 9).

10. EFFECT OF THE VELOCITY GRADIENT DURING RAPID MIXING ON THE EFFICIENCY OF COAGULATION

The influence of increased water alkalinity on the efficiency of the physical and chemical processes concomitant with coagulation (which manifests itself in more

efficient hydrolysis of the coagulant and consequently in less effective organic matter removal, e.g., in the Oława water samples) proves how important are the first seconds following the addition of the coagulant. What we have in mind is the effect of such parameters as the velocity gradient during rapid mixing, coagulant concentration and coagulant type.

When use is made of aluminium sulphate, aluminium chloride or Fe(III) coagulants, the velocity gradient during rapid mixing plays an important role. The plots in figure 10, which illustrate the efficiency of COD_p removal obtained for different gradients of the Odra water samples, depend on the Ca/Mg ratio and are similar (curve 1 and 2) to the plots in figure 3. The relations mentioned above were determined for a gradient (G) ranging between 165 s^{-1} and 465 s^{-1} . Thus, for $G = 58 \text{ s}^{-1}$, the relation is linear and increases with the increasing value of the Ca/Mg ratio (figure 10). The efficiency of COD_p removal achieved for this gradient at a low Ca/Mg ratio is on an average by 15% lower than that obtained for the highest gradient investigated.

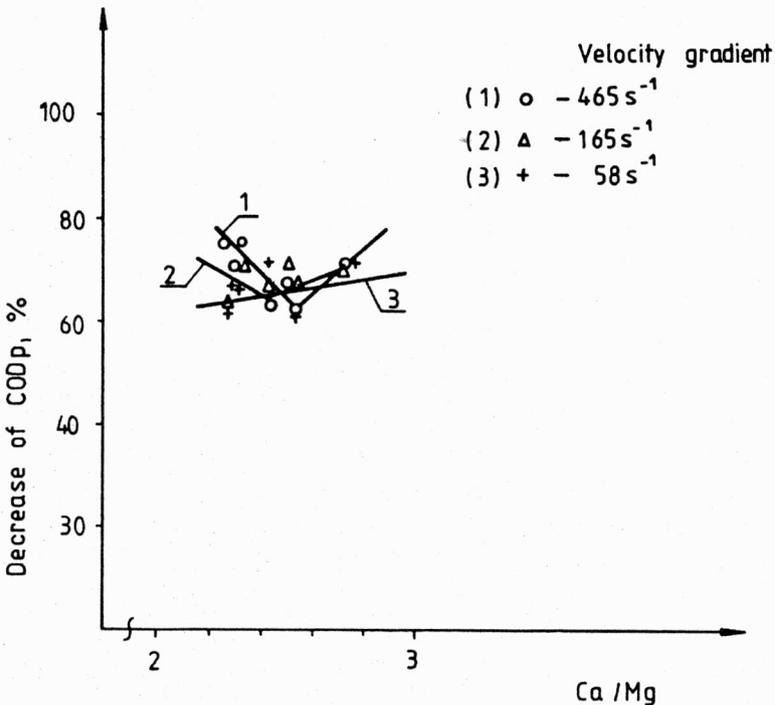


Fig. 10. Effect of the velocity gradient on COD_p removal ($D_{\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}} = 100 \text{ g/m}^3$)

The application of the rapid mixing procedure limits the occurrence of regions with increased coagulant concentrations which increase the degree of conversion with the increasing water alkalinity, thus enhancing hydrolysis and decreasing the effi-

ciency of organic matter removal at the same time. The minimum efficiency of hydrolysis determined on the basis of alkalinity decrement in the way shown above varied from 88 to 72% for the minimum Ca/Mg ratio values and for the 58 to 465 s⁻¹ velocity gradient range.

11. CONCLUSIONS

Coagulation with iron- or aluminium-based coagulants involves direct reactions with humic substances, yielding a high destabilisation of the latter. In this way, a high efficiency of organic matter removal can be achieved. But there are also competitive reactions concomitant with the hydrolysis of the coagulant; they are likely to produce positively charged colloidal systems, which provide destabilisation of humic substances on the principle of the oppositely charged colloid. In that particular case, the removal efficiency for organic pollutants is much lower because the colloids are destabilised in an indirect way. These reactions are influenced by the Ca/Mg molar ratio. Extreme values of the Ca/Mg ratio for the investigated riverine water samples create favourable conditions for direct reactions of the coagulant with humic substances, whereas Ca/Mg ratio values approaching those of the calcium–magnesium equilibrium in the humic complex provide conditions for competitive reactions.

Favourable conditions for competitive reactions are also created by increased water alkalinity (as it was in the case of the Oława river water samples).

The adverse effect of competitive reactions on the removal of organic pollutants can be inhibited by selective dosage of inert calcium or magnesium salts.

To improve the efficiency of humic acid removal it is advisable to apply two coagulants – an aluminium-based one and an iron-based one – to the same water. The application of an aluminium-based coagulant is appropriate when the Ca/Mg ratio takes low values. For the increased values of Ca/Mg ratio, the use of a ferric coagulant is recommended.

The efficiency of coagulation is also influenced by the velocity gradient value during rapid mixing. When the Ca/Mg ratio is low, the gradient value should be greater than 300 s⁻¹.

If there is a need to reduce the adverse effects of competitive reactions, the application of the optimum coagulant dose, established by taking into account not only the pollution level but also the alkalinity of the water to be treated, might be of crucial importance.

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WPLYW FIZYKOCHEMICZNYCH PROCESÓW NA KOAGULACJĘ SOLAMI GLINU LUB ŻELAZA(III) ZANIECZYSZCZEŃ WÓD POWIERZCHNIOWYCH

Procesom koagulacji zanieczyszczeń wód powierzchniowych koagulantem glinowym i żelazowym towarzyszą bezpośrednie reakcje z substancjami humusowymi. Reakcje te charakteryzują się dużą skutecznością destabilizacji, a więc i dużym stopniem usuwania zanieczyszczeń organicznych. Oprócz tych reakcji przebiegają reakcje konkurencyjne, związane z hydrolizą koagulantu. Prowadzą one do powstania dodatnio naładowanych układów kompleksowych. Skuteczność usuwania zanieczyszczeń organicznych w wyniku reakcji konkurencyjnych jest dużo niższa, gdyż destabilizacja koloidów odbywa się w sposób pośredni.

Udział obu typów reakcji zależy od wartości stosunku molowego Ca/Mg. Ujemny wpływ reakcji konkurencyjnych można wyeliminować lub ograniczyć przez selektywne dawkowanie obojętnych soli wapnia (np. CaCl_2) lub magnezu (np. MgSO_4). Podobny efekt uzyskuje się, selektywnie stosując dwa koagulanty – glinowy i żelazowy. Duża intensywność mieszania (gradient prędkości ruchu cieczy $G > 300 \text{ s}^{-1}$) oraz optymalna dawka koagulantu pozwala również ograniczyć te niekorzystne zjawiska.