Experimental-theoretical substantiation of the previously formed sediment’s application as the water clarification process intensifier

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Abstract. An attempt was made to experimentally and theoretically substantiate the use of the previously formed sediment for clarifying water. The water-pipe sediment contains a large amount of aluminum sulfate, which, when introduced into water, promotes hydrolysis, sorption, and adhesion. When the recommended doses of spent sediment are introduced into water before entering the sedimentation tanks, the suspension is destabilized, most of it falls into the sediment, and the remaining destabilized part is exposed to the coagulant introduced sometime after the sediment is introduced, which contributes to the renewal of the suspension activity in the sorption and adhesion phenomena. In addition, the sediment recycling process can be considered as sorption. The electro kinetic potential is in the range of 15-20 mV using the sediment recirculation method.

In domestic and foreign literature on the sediment reuse from the sewage treatment plants, there is practically no theoretical justification for their influence on the coagulation process in the natural waters’ treatment.

Therefore, we made an attempt to experimentally and theoretically substantiate the advisability of introducing sediment from the horizontal sediment tanks into the clarified water.

For the theoretical justification of the sediment recirculation process, the presence of residual adsorption-adhesive ability of aluminum hydroxide in the formed sediment after the time of its contact with the treated water in the sediment tank has been established.

It was previously proved that the process of using coagulant in structures does not proceed completely. The completeness of the reagent use for water treatment depends on a number of factors:

- physical and chemical features of water and reagent treatment;
- temperature conditions of the flocculation process;
- mass transfer conditions in the process of mixing the reagent with the processed water and its movement in the structures’ working area.

Let us consider in more detail the water coagulation process with aluminum sulfate (alumina sulfate) - the most common coagulant.

When aluminum sulfate is introduced into water, its molecules dissociate:

\[ \text{Al}_2\cdot (\text{SO}_4)_3 \leftrightarrow 2\text{Al}^{3+} + 3\text{SO}_4^{2-} \] (1)
The trivalent aluminum cations formed as a result of dissociation enter into chemical interaction with the substances present in water. In this case, a partial decrease in the colloidal clay system stability can occur due to the exchange for clay and divalent cations for trivalent cations $\text{Al}^{3+}$.

The process of the suspension particles’ ion exchange [1] proceeds quickly and ends when the exchange capacity of the suspension particles is exhausted and equilibrium is established between cations in the adsorption layer of clay particles and in solution. Next is the hydrolysis of the excess aluminum sulfate added to water with the intermediate compounds’ formation, resulting in a colloid of sparingly soluble aluminum hydroxide:

$$
\text{Al}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_3 + 3\text{H}^+
$$

(2)

The hydrolysis completeness is estimated by the constant and hydrolysis degree. In the hydrolysis of cations in the first step (1) and if the equation is presented in a modified form, then:

$$
\text{Kt}^+ + \text{H}_2\text{O} \leftrightarrow \text{KtOH} + \text{H}^+
$$

(3)

That according to the law of the acting masses can be written.

\[ R_r = \frac{[\text{KtOH}][\text{H}^+]}{[\text{Kt}^+]} \]

(4)

where: $\text{Kt}$ – is the concentration of aluminum cations, $R_r$ – defines the hydrolysis rate constant.

The hydrolysis rate is proportional to the coagulant cations’ concentration:

$$
V = R_r [\text{Kt}]
$$

(5)

Since the concentration of coagulants used is low, in this case – $\text{Al}_2(\text{SO}_4)_3$, then we can assume that their hydrolysis rate is proportional to the amount of salt introduced.

From equation (4) it follows that with an increase in the hydrolysis constant R, the equilibrium shifts toward the formation of sparingly soluble aluminum hydroxides and the hydrolysis proceeds more fully.

The positively charged polynuclear aluminum hydro-hydroxy-complexes formed by the coagulant hydrolysis — micelles and larger spherical sol aggregates, as well as the less polymerized hydro-hydroxy-complexes are chemisorbed on the clay surface or other mineral particles of the treated water. In this case, an interaction with the hydration shell of a clay particle occurs with the formation of hydrogen bonds and at the same time the charge is neutralized. As a result, the suspended particles are coated with a dense layer of aluminum hydroxide particles [2].

The hydrolysis degree, which characterizes the hydrolysis reaction completeness, should increase with increasing temperature and pH of the dispersed system, diluting the solution (reducing the dose of coagulant) and decreasing the solubility of the hydrolysis products - aluminum hydroxide.

When opacifiers are introduced into water, heterogeneous particles are involved in coagulation. Thus, opacifiers play the role of a surface, provoking the first stages of adsorption-coagulation interaction, and contribute to the denser aggregative structures’ formation. Due to the large number of crystallization centers, the structure is less branched and denser.

Therefore, particles coated with small particles of aluminum hydroxide can combine with each other, forming dense flakes, in which case a lower consumption of reagent will be required. Hydroxide particles cover the surface of more particles (in this case, the added opacifier is a sediment) and stick together with each other in a chain, forming a spatial lattice, inside which trapped water is located. Colloidal impurities are adsorbed on the outer and inner surfaces of the flakes.

When treating water with coagulants, many researchers noted the important role of sorption phenomena [3, 4-6]. Obviously, such sorption phenomena will occur during sediment recirculation. In this case, several processes will take place simultaneously [7]:

- exchange adsorption;
- adsorption of coagulant hydroxides on coarse water impurities.
- adsorption of ions, molecules and micelles of various chemical composition on aluminum hydroxide.

During the adsorption of coagulant cations by impurity particles, they exchange cations forming a diffusion layer of counterions ($\text{K}^+$, $\text{Na}^+$) on ions $\text{Al}^{3+}$ or $\text{Fe}^{3+}$. 

The particles of impurities stabilized as a result of exchange adsorption do not form sufficiently large and strong flakes upon sticking. Therefore, if exchange adsorption is significantly manifested, the physical parameters of the flakes deteriorate. Obviously, it is necessary to ensure a decrease in metabolic adsorption in some way. This can be achieved by introducing a formed sediment into the treated water, as a result of which a certain mass of finely dispersed impurities will be adsorbed on its coarse flakes.

As a result, the number of small flakes will decrease, which in turn will provide a more complete effect of water clarification. The simultaneous concentration of the coagulating substance electrolyte on the sediment flakes contributes to the formation of a new solid phase, accelerating the process of flocculation and clarification of water in general.

The adsorption of ions, molecules and micelles of organic origin on the coagulant hydroxide is gradually reduced and the process of bleaching water stops. In this regard, the use of a sediment having a free part of coagulant hydroxide has a positive effect on the bleaching process by adsorbing a part of organic impurities or coagulant hydroxide on a sediment with substances that cause water color to be adsorbed on it.

The flocculation effect increases significantly when impurities adhere to coagulated flakes, i.e., during adhesion.

The adhesion forces between the particles are usually determined by the method of professor Kurgaev E. F. [8], in parallel with the experiments to study the sediment gravitational compaction process.

When the previously formed sediment, which is a large flake, is introduced into the treated water, an improvement in the flocculation process can be expected, since the probability of the particles’ collision in a polydisperse system is greater than in a monodisperse system. It was established that the probability of a small particle colliding with a large one is greater than the probability of two small particles connecting together [3].

Hans Muller suggested that there are two kinds of particles in a colloidal solution i and k with radii Gi and Gk. Let a particle with a radius Gi >> than Gk. Adhesion can occur only in contact of i and k. Therefore, the action radius of such particles is Rik = Gi + Gk.

From this it follows that the probability of a small particle falling into the sphere of attraction is large will be equal to:

\[ W = \frac{2}{3} \frac{kT}{\eta} \cdot \frac{R_{ik}}{2} \cdot \left( \frac{1}{G_i} + \frac{1}{G_k} \right) \]  
(6)

where: \( W \) – shows the probability of a small particle falling into the sphere of attraction of a large;
\( T \) – is absolute temperature;
\( K \) – is the Boltzmann constant;
\( \eta \) – defines water viscosity.

The probability of a small particle entering the scope of another small particle will be equal to:

\[ W_{kk} = \frac{4kT}{3\eta} \]  
(7)

The ratio of these probabilities will be:

\[ \frac{W_{ik}}{W_{kk}} = \frac{(1 - G_i / G_k)^2}{4G_i / G_k} \]  
(8)

Knowing that G_i / G_k > 1 always and the probability is W_{ik} / W_{kk} Moreover, the probability of a small particle collision with a large one increases with the growth of the difference in size, the presence of large particles disappears much faster than without it.

Deryagin B.V. [9] and others showed that the adhesion rate of the small particles to the large particles is approximately 400-500 times greater than the rate of the small particles’ adhesion to the small particles.
The change in the number of large particles can be determined by the Smoluchowski equation [2]:

\[ v = v_0 \left( 1 + \frac{\tau}{\theta} \right) \]  

(9)

where: \( v_0 \) – is the initial numerical concentration of particles.

The change in the number of small particles can be determined by the Mueller equation:

\[ v = \frac{v_0}{1 + \frac{\tau}{\theta}} \left( \frac{V_r}{2} \right)^{\frac{\tau}{\theta}} \left( 1 + \frac{\tau}{\theta} \right)^{\frac{V_r}{2}-1} \]  

(10)

where: \( V_r = R/r \) – is the ratio of large and small particles.

As follows from these two equations, the change in the number of small particles is faster than change in the number of large particles. The introduction of large particles into the disperse system (a cloud of colloids, anion exchangers are already being covered with a hydroxide coat) leads to the disappearance of small particles, and the sooner, the larger is the difference in their sizes \( V_r \). At \( V_r \) the colloidal system turns into a monodisperse system and equation (9) turns into the Smoluchowski equation (9). At the same time, the larger spherical particles’ formation of the aluminum hydroxide sol, including the spent part of the sediment, occurs. Coagulation of large particles due to their lower partial concentration proceeds more slowly with the loose structures’ formation.

When the opacifier is introduced into the treated water, the particles are combined with each other, forming denser flakes, already being covered with a “hydroxide coating”. In this case, a lower consumption of coagulants should be required [2].

An analysis of the physicochemical processes of water purification and the influence of the previously formed sediment on these processes showed that the use of sediment can have a positive effect on hydrolysis, sorption and adhesion, and therefore, on the coagulated suspension physical parameters’ improvement.

Suspended substances contained in the water of the southern rivers consist mainly of the mineral origin particles, which are the hydrophobic impurities. Saturated bonds predominate on the hydrophobic surfaces and therefore these surfaces are almost devoid of hydration shells.

Fine and colloidal hydrophobic particles have a large specific surface on which ions in water are adsorbed. Colloidal particles directly adjacent to the nucleus form an adsorption layer. In this layer there is also a certain number of ions with a sign opposite to that of surface-nuclear ions, but not compensating for the charge of the latter. Around the core of the particle with an adsorption layer (granule) a diffusion layer is created from counterions that compensate for the granule charge.

A colloidal particle, together with its surrounding diffuse layer, is called a micelle. At rest, the micelle is electrically neutral, but being in a Brownian motion, colloidal particles move together with the adsorption layer, the counterions of the diffuse layer lag behind the granule and the colloidal particle is electrically charged. The magnitude of the electric charge is equal to the electro kinetic potential - the zeta potential. As a rule, all particles of a given colloidal system have a charge of the same sign, which causes their mutual repulsion and interferes with enlargement. With a decrease in the electric charge of the particles, i.e., with a decrease \( \xi \) – potential, repulsive forces are reduced and the process of the colloid coagulation becomes possible. The state of the colloidal system with \( \xi=0 \) is called an insulating state, and the quantity pH, corresponding to this state is called the isoelectric point of the system.

Some authors [10, 11] investigated the suspended solids’ concentration and dispersion effect on the zeta potential value. They proved that the zeta potential independence does not depend on the dispersion of particles, increase with increasing number of suspended solids up to 60 mg / dm³, constant value in the range of 60-500 mg / dm³ and a decrease in zeta potential at the suspended solids concentration of more than 5000 mg / dm³. The dispersion medium was the water of the river Don, Kura, Aksai. The larger are the value of the zeta potential of the particles, the more difficult it is to ensure its adhesion with other fine particles, coarsening as well as their deposition.

According to the Schulze-Hardy rule, the ability of an electrolyte to cause coagulation of the colloidal system grows extremely rapidly. For the positively charged colloids, anion exchangers are the coagulating ions, and for the negatively charged colloids - the cations.
Along with this, the scientists [12] calculated the values of the coagulation rate constants. It indicates that the coagulation rate of a system is greatly influenced by the size distribution of particles. The rate of association of the relatively small particles (5-10 μm) with the larger ones (50 μm) in a turbulent flow can be several orders of magnitude higher than the rate of association of only small ones.

At the same time, between the colloidal particles there are the molecular forces of mutual attraction of the van der Waals. The attractive forces, as well as the forces of mutual repulsion of the same charged colloidal particles, manifest themselves most intensively when the particles approach each other [13]. In this case, the initial repulsive force is greater than the attractive force and the particles repel each other. If particles, under the influence of the kinetic energy of their motion, have overcome the “force barrier”, then the attractive forces become dominant and the particles stick together. However, the need for large kinetic energy of particles to overcome the repulsive forces reduces the likelihood of particles sticking together and coagulation of the colloid, the colloidal system retains its aggregative stability.

To ensure the conditions for the flakes’ formation forming a sediment from the mass of fine and colloidal particles in the water purification technology, the electrolyte concentration in water is increased. In this case, the following processes occur in a short period:
- the electrolyte concentration in water increases, which leads to a decrease in the particle charge due to the addition of additional counterions to the diffuse layer of micelles;
- if the added electrolyte has a charge of particles opposite to the charge of water-polluting particles, then mutually neutralizing the oppositely charged particles of suspension and coagulant occurs, which leads to a loss by these particles of resistance to adhesion, to enlarge them;
- the electrolyte is hydrolyzed in water with the flakes’ formation, on which water impurities are adsorbed. In turn, the coagulant chains can adhere to the surface of large impurities, during the deposition of which water is clarified.

Therefore, with reagent clarification of low-turbid waters in the first stage, the coagulating electrolyte concentration is still insufficient to cause coagulation of small particles. Sorption of colloidal hydroxide on the surface of suspended particles is nothing more than the adhesion of very small and very large particles. It is known from practice that the presence of coarse suspension in water accelerates the coagulation rate of a system is achieved by introducing an opacifier into water.

Thus, the suspended solids (opacifier) play the role of a surface that provokes the first stages of adsorption-coagulation interaction and contribute to the dense aggregated structures’ formation.

In accordance with the Muller’s autocatalytic theory [14] for polydisperse systems, the particles of different sizes aggregate rather than the particles of the same size. This is especially true if the sol particles differ in size by 30–40 times or more, which is different in the case of water purification with aluminum sulfate.

The introduction of large particles into a dispersed system leads to the small particles’ disappearance, and the sooner it happens, the larger is the difference in their sizes.

The treatment of low-turbid waters by sediment recirculation accelerates the solid particles’ aggregation process.

We conducted the studies on the recommended effect for settling the doses of aluminum sulfate on the zeta potential of the suspension particles, as well as the study of the effect of the aluminum sulfate recommended sedimentation doses on the zeta potential value of the suspended particles formed during the water treatment by recirculating the sediment.

In accordance with the electrical phenomena classification, there are devices of various designs to determine the colloids’ zeta potential. The action of these devices is based on changing the parameters of electro kinetic phenomena. Subsequently, on the basis of the theory linking these parameters with the zeta potential, its value is determined.

The studies were carried out by the microelectrophoresis method, based on direct observation under a microscope of the suspension individual particles’ movement under the influence of a constant electric field in a special chamber. By measuring the particles’ speed of the electrophoretic movement in the system with a potential gradient of the applied voltage and knowing the values of the viscosity and
dielectric constant of the liquid, the zeta - particle potential (mV) can be calculated using the Stoltz-Smoluchowski formula:

\[
\zeta = \frac{4 \pi \eta \lambda U}{\varepsilon E} \times 10^{-2}
\]

where: \(\xi\) – zeta – is the solid phase potential;
\(\eta\) – is the dispersed phase dynamic viscosity, mPa \cdot ^\circ\text{C};
\(L\) – is distance between electrodes, cm;
\(E\) – defines the potential difference at the electrodes;
\(\varepsilon\) – is the absolute dielectric constant of a dispersed medium;
\(U\) – is the microscopic observation electrophoretic particle velocity, cm / s;

\(U\) = mains voltage (210-250) 220 V
distance between electrodes 9 cm

where: \(\omega\) – is the electrophoretic velocity of particles equal to 10 cm\(^2\)/V \cdot c
\(\omega = \frac{U}{H}\)
\(U = \frac{S}{T}\)

where: \(S\) – is the distance of electrophoretic mobility of particles, cm (2778\(\cdot\)10\(^{-5}\) cm);
\(T\) – is the travel time, C;
\(H\) – is the electric field potential gradient, V / cm.

The studies were conducted three times with the initial turbidity in the range of up to 10 mg / dm\(^3\) and from 10 to 20 mg / dm\(^3\), the zeta potential was determined and then the average value was found.

The experiments’ results to determine the electro kinetic potential magnitude show that the low effect of water clarification without the reagents use is due to the fact that the electro kinetic potential magnitude increases and, accordingly, the particles repel each other and maintain aggregative stability. The increase in the zeta potential for the suspended sediment untreated with reagents can be explained by the fact that the amount of suspended solids decreases. In this case, an increase in the diffuse layers, the remaining particles, and, accordingly, an increase in the charge.

When water is treated with aluminum sulfate with the introduction of its optimal dose, the electro kinetic potential decreases by 20%, which leads to the aggregate stability loss of the suspension, particle adhesion and a rather good effect of water clarification. This is confirmed by the results of the laboratory experiments, which show that with the recommended optimal doses of coagulant and the settling time of at least 60 minutes, the amount of suspension in clarified water (purified Don water) is less than 10 mg / dm\(^3\).

When treating water with a coagulant in combination with sediment in the ratio \(D_r/D_k = 1\), with the condition of introducing the optimal dose of the coagulant, the value of the electro kinetic potential decreases by 30%, which in turn leads to the aggregate stability loss, but when compared to the water purified by one coagulant, the value of the electro kinetic potential is lower. Obviously, this is due to the relatively high dose of sediment for water treatment.

When clarifying water with a coagulant in combination with sediment in the ratio \(D_r/D_k = 0.75\) with the condition of introducing the optimal dose of the coagulant, the value of the electro kinetic potential decreased by 325, which ultimately led to the loss of aggregative stability, particle adhesion and a high-water clarification effect.

With equal doses of coagulant 20-30% from the optimal dose and introduction of it in combination with sediment in the ratio \(D_r/D_k = 1.0\); 0.75 the value of the electro kinetic potential decreases by 50%, which leads to a high effect of clarification of water.

In light of the foregoing, the fact of a decrease in the optimal doses of coagulant compared with the recommended Building Code [15] entered before the horizontal sediment tanks can be explained. They are the first stage of natural water purification if the incoming water contains a relatively small amount of suspended solids (up to 10 mg/dm\(^3\) from 10 to 20 mg/dm\(^3\); 20-40 mg/dm\(^3\); 40-70 mg/dm\(^3\); 70-150 mg/dm\(^3\)).
Summary

It can be seen from the foregoing that when the recommended doses of spent sediment are introduced into water, sediment destabilizes most of it sediments before entering the sedimentation tanks, and the remaining destabilized one is exposed to a coagulant introduced sometime after the sediment is introduced, which contributes to the suspension activity renewal in sorption phenomena and adhesion. In addition, the sediment recycling process can be considered as adsorption [3].

The analysis of the results obtained in the laboratory cycle of experiments with the determination of the electro kinetic potential shows that the effect of water clarification with various combinations of reagents, also at different ratios $D_r/D_k$ directly proportional to the magnitude of the electro kinetic potential.

Electro kinetic potential is in the range of 15-20 mV using the sediment recirculation method.

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