HIGH EFFICIENCY TITANIUM COAGULANTS FOR WATER TREATMENT

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Abstract: Titanium compounds are very perspective reagents for water treatment because of their many outbreaking benefits compared to traditional coagulants – smaller dosage, lesser pH-dependency, they are biologically inert, work at low water temperature. But they have some technological issues, preventing them from wide use. One of the ways to overcome this issues shown in this article. Results of use of nanoencapsulation of Ti(IV) salts into solvable cells shown. This way allows to overcome problem with too quick hydrolysis and evenly distribution of coagulant in treated water. Also titanium coagulant was practically compared to traditional coagulant to show benefits of titanium-based coagulants.

Keywords: titanium, coagulant, hydrolysis, water treatment, low temperature, high color.

1. Introduction

Titanium coagulants in water treatment – are something like a holy grail. They give a lot of benefits, beating out all other types of existing coagulants, but have a lot of technological problems to get their way from labs to water treatment technology.

First of all, ion of Ti^{4+} have bigger charge, than ions of Al^{3+} and Fe^{2+} (usually used as coagulants), what, as we know from colloidal chemistry, draws it as much better coagulating agent (bigger charge of coagulating ions – less ions needed to compensate dzeta-potential of colloidal particle – less dose of coagulant required for sedimentation). So dose of titanium coagulant in the same circumstances should be significantly lesser, than of aluminium or ferrum coagulant.

Second thing about titanium-based coagulants – Ti^{4+} hydrolysis (**Fig. 1**) begins at much lesser pH, than hydrolysis of Al^{3+} (**Fig. 2**).

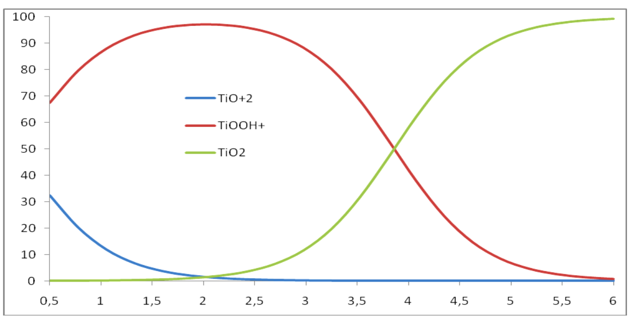


Fig. 1. Species-pH distribution of Ti(IV) compounds in water. Total Ti(IV) concentration – 3×10^{-4} M/dm^3

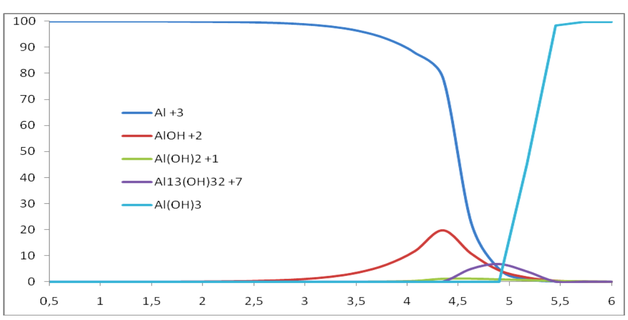


Fig. 2. Species-pH distribution of Al(III) compounds in water. Total Al(III) concentration – 3×10^{-4} M/dm^3

As we can see from this figures, hydrolysis of Al^{3+} (and forming of flocks) begins at pH 4.5. It well corresponds with practically known fact, that aluminium-based coagulants do not work at all if pH of treated water less than 5.

On the other hand, hydrolysis of Ti^{4+} begins at much lesser pH, so coagulation process with Ti(IV) compounds could form flocks at pH 3 and even less.

Other benefit of Ti(IV)-based coagulants – titanium and it's compounds are found biologically inert, so water, containing Ti(IV) compounds is safe and residual concentrations, greater than MAC, do not cause Alzheimer's disease (like in case with aluminium coagulants) or haemochromatosis (like in case of ferrum-based coagulants).

But there is one thing, that stands between Ti-based coagulants and their application in practice: Ti(IV) compounds hydrolyzes in water so quickly, that coagulant can't be distributed well in water, what causes a lot of technological problems to apply Ti-based coagulants in full-scale water treatment plants.

2. Methods

One of the ways to evade this proposed by Stremilova et al. They proposed to use complex coagulant of aluminium(III) salts and TiO_2 (up to 10 % mass). Addition of Ti(IV) oxide to aluminium coagulants significantly improve activity and decreases dosage (especially at low temperatures, when pure Al(III) coagulants almost stop working), but actually Ti(IV) compound in this solution works not as a coagulant, but as a turbidizer, particles of which helps to form flocks.

We choose other way to work with Ti(IV) compounds – synthetic compositions to temporary slow down Ti^{4+} hydrolysis during application. It allows technologically appropriate application of Ti(IV) salts to treated water, allowing them to distribute well and effectively coagulate wastes. The idea was to place nano-size particles of titanium salts into water-soluble compound, which forms shell around titanium salt, preventing it for some time (until shell compound dissolves in water) from reaction with water.

This approach gives several benefits.

First of all, particles of coagulant very small (with size up to tenths of nanometers) that allows to distribute coagulant in treated water more evenly than in case of use of titanium salts by themselves or usage of complex coagulant with addition of TiO_2.

Other benefit of this approach is that we could "program" coagulant to properties we need – varying size of titanium salt drop, material and thinness of shell. For example, if we need to increase time, needed for even distribution, we need only to increase amount of protective compound during synthesis.

Also, using this approach, we could use not only titanium salts, but oxy-salts, which decrease demand of alkalinity for proper treatment. Other approaches do not allow to use oxy-salts, because final hydrolysis appears too quickly and we obtain huge particles of TiO_2, with uneven distribution in treated water.

3. Results

Obtained titanium coagulant was exposed to jar tests in comparison with traditional aluminium coagulant. Initial conditions of tests were same (Color: 102°, turbidity: 0,2 mg/dm^3, temperature 12 °C, pH=7.38). Such conditions are quite extremal and were chosen because water with high color and low turbidity is the most problematic for coagulation. Also, traditional aluminium coagulants works well in warm water, but fails at low temperatures. Results of jar tests shows, that titanium coagulant works better than aluminium and same results could be obtained at much smaller doses (**Fig. 3**). Same results could be obtained with dose of titanium coagulant 100 times smaller, than aluminium coagulant.

Visual comparison (**Fig. 4)** shows, that in case of titanium coagulant flocks appear more quickly and much larger in size, so they precipitate more quickly and easily.

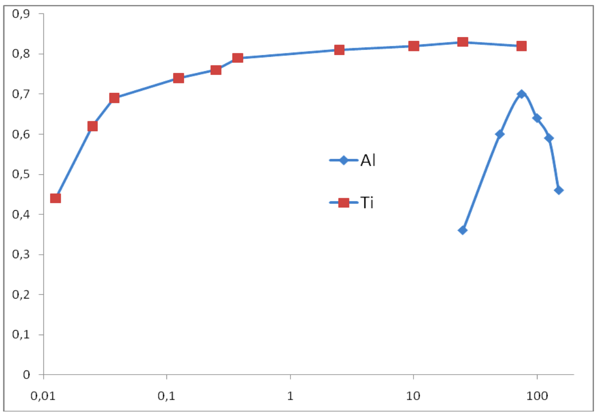


Fig. 3. Dose-treatment degree (color) curves of titanium- and aluminium-based coagulants. PH=7.38.
Dose scale is logarithmic

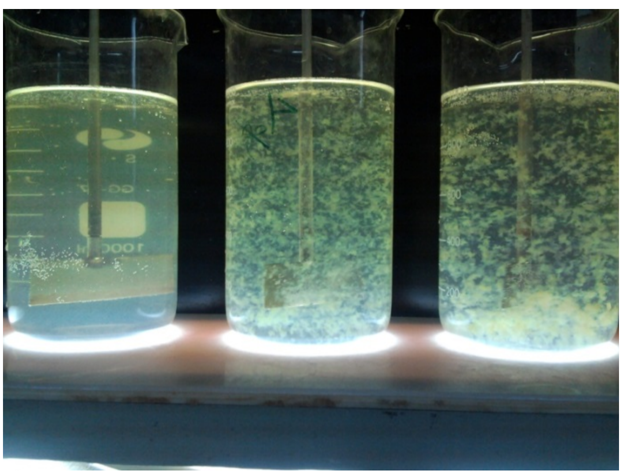


Fig. 4. Flocks during jar test. From left to right: Al 75mg/dm^3; Ti 0,375 mg/dm^3; Ti 2,5 mg/dm^3

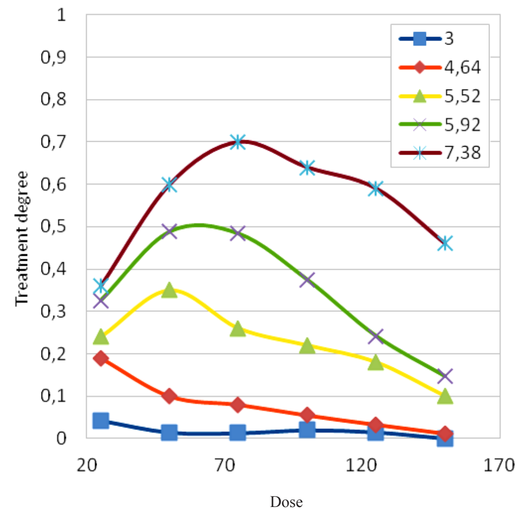
If aluminium coagulant forms flocks for about 20 minutes and average size of flocks about 1 mm, in case of titanium coagulant flocks appears in 1-2 minutes and their average final size is up to 10–15 mm.

As it said before, one of the benefits of titanium salts – they should work at lower values of pH, than aluminium salts.

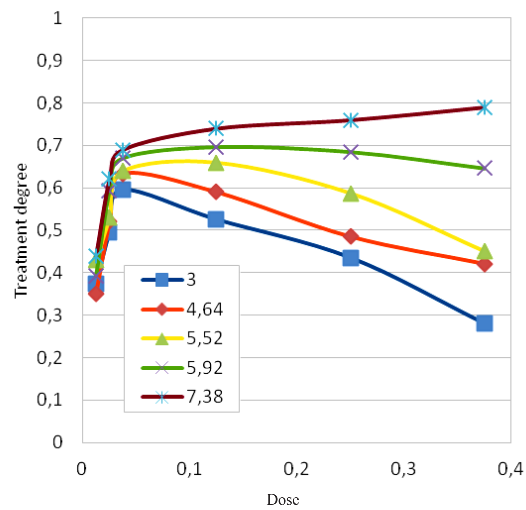
To study influence of pH several additional jar tests were done. Initial conditions were the same, but pH were corrected by addition of diluted HCl. Buffer solutions were not used to eliminate influence of additional compounds being placed to treated water.

Results of jar tests performed with aluminium coagulant shows, that effectiveness of coagulation significantly decreases with fall of pH (**Fig. 5**).

If at pH higher than 7 aluminium coagulant could remove up to 70 % of gumic acids (which responds for color), but at lower pH degree of treatment degrades significantly and at pH lower than 5 it almost not working.



a



b

Fig. 5. Influence of pH on degree of treatment:
a – aluminium coagulant; *b* – titanium coagulant

As seen on figure, in all cases titanium coagulant gets higher degree of treatment and works satisfactorily even at pH=3.

Effectiveness of coagulation falls with decrease of pH in both cases (either aluminium or titanium coagulant), but in case of titanium it falls much slower and titanium coagulant remains effective in all range.

Other benefits of titanium coagulants are their lower alkalinity demand and lesser pH change at water treatment.

Results of pH change (as a result of coagulation) measuring shown on **Fig. 6.**

Coagulation with aluminium coagulant results in significant change of pH – so if we want to obtain appropriate water treatment, we need to add lime to correct pH and prevent dissolvation of flocks.

In case of titanium coagulant change of pH significantly smaller, what means, that in most cases we need no pH correction. Also, because of high hydrolysis constants flocks more stable, than in case of aluminium coagulant, so pH correction needed only in case of strict requirement to pH of treated water.

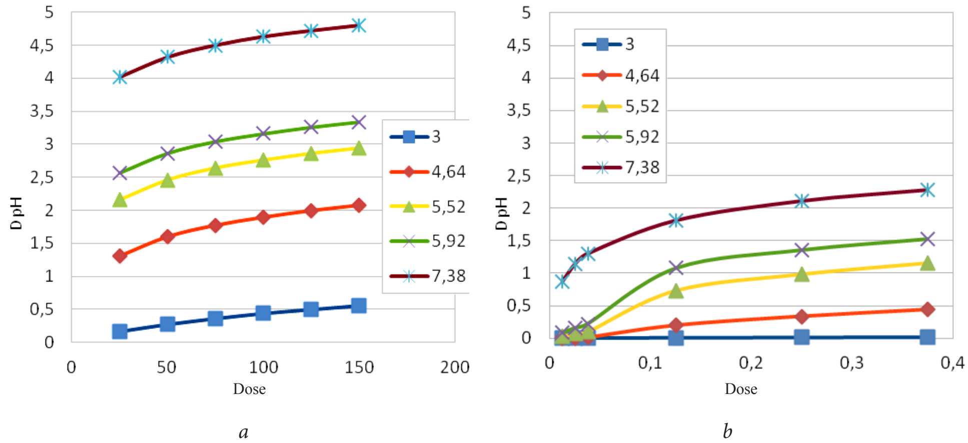


Fig. 6. Change of pH in result of coagulation: *a* – aluminium coagulant; *b* – titanium coagulant

4. Conclusion

Titanium coagulants, based on nano-encapsulation of titanium salts allows to obtain much better results than in case of traditional coagulants, even in case of extreme conditions. They solves main disadvantages of titanium salts and titanium dioxyde.

Results of jar tests shown, that with use of Ti-based composition much better degree of treatment could be achieved even in complicated conditions, and effective dose of Ti-based coagulant is several times less, than dose of Al-based coagulant. Also, because of smaller dosage, pH decrease much smaller in case of Ti-based coagulant – it means, that this coagulant could be applied to water with low alkalinity without need to add lime.

This approach still in development, but current results show, that Ti-based coagulants could be used in water treatment in near future.

Also there is a patent (UA 109947, 2015) obtained on some techniques of this approach.

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