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APPLICATION OF THE ORGANIC ACIDS SOLUTIONS FOR CLEANING THE MEMBRANE BLOCKS OF BAROMETRIC INSTALLASTIONS

Paper describes the experimental studies, using the solutions of food acids for the extraction of the iron compounds from the membrane blocks of barometric installations by means of maceration. Ferric iron compounds are typical and at the same time complex pollutants of the membrane blocs. Iron norms exceedance in the water may provoke allergic reactions and organic iron may cause stomach and duodenal ulcer. High concentration of iron in the water creates favorable conditions for the development of iron bacteria, especially in the warm water. Waste products of iron bacteria are canrcinogens.

Aim of the given research is searching of the optimal means of the membrane block cleaning from the ferric iron compounds. It is worth taking into account that this method must be ecologically safe and economically expedient that enables to use it in practice, increasing the service life of the membrane block of the units for barometric membrane purification of water.

Thus, after the analysis of the scientific sources, the decision was made to use the solution of hydroxy-succinic food acid for the elimination of the iron compounds from the surface of the membrane blocks. In the laboratory conditions the study of the efficiency of hydroxy-succinic acids solutions (malic acid formula, $C_4H_6O_5$) and methane carboxylic (acetic acid, formula $C_2H_4O_2$) acids impact on the extraction of Fe^{3+} ions was performed. A number of experiments were carried out, observation and assessment of optical density measurements of the standard and working solutions was performed at photo-colorimeter, clarification, filtration, preparation of the work solutions with malic and acetic acids. Identical experiment was performed, using citric acid but it did not give the desired results.

Results of the studies were summarized in the Table 2 and conclusions were made that the solution of dibasic 6% acid $C_4H_6O_5$ is more efficient for fighting the precipitation of the compounds of the ferric iron on the membrane blocks of baromembrane water treatment units. This method is suitable for application in real conditions as the food solution of the malic acid is ecologically safe, financially accessible and in case of corresponding dilution can be discharged into the common drain, it also gives better results at short-term maceration.

Key words: *baromembrane units, membrane blocks, membrane pollutants, malic acid, acetic acid, photocolorimetry.*

Introduction

Installation for baromembrane purification of water is efficient and simple method to obtain potable water from the sea water, impure water, technological water or tap water of any content. With the development of technologies, growth of population of the planet and decrease of the sources of the freshwater such installations become more and more popular. It is known that these installations are easy to operate, sufficiently automated, cost efficient, consume small amount of energy and have numerous modifications, depending on the sphere of usage and qualitative and quantitative composition of the input water. However, such installations have considerable drawback, this problem has not been solved up till now – each 2 – 3 years the membranes which are main cleaning element of baromembrane installations must be replaced.

That is why, the important task for today is the search of the methods to increase the service life of the membrane blocks, performing cleaning from impurities, accumulated on the surface of the membrane blocks, in the pores of membranes, etc. Such impurities comprise [1]:

– calcium carbonate (chalk);
– calcium sulphate (gypsum), barium sulphate and strontium sulphate;
– ferrous oxides, manganese oxides, copper oxides, nickel oxides, aluminium oxides;

– polymerized silicon;
– inorganic/organic or mixed colloid depositions;
– organic depositions of the natural origin;
– artificial organic compounds, such as antiscalants, dispersants, cation polyelectrolytes;
– microbiological depositions such as sea-weeds, mildew, etc.

One of typical and at the same time complex pollutants of the membrane blocks are compounds of the ferric iron. It is known [2], iron is in the form of ferrous iron in the underground waters and in the surface waters it is oxidized to ferric iron, is hydrolyzed and creates poorly soluble precipitation of ferric hydroxide which is in the water in state of colloidal solution. That is, ferric iron is in the water, supplied for the purification in the form of Fe^{3+} ions and products of their hydrolysis. Iron is presente practically in all underground and surface waters of the planet. That is why, it is quite clear that iron is one of the basic and constant pollutants of the membranes of baromembranes installations, used for water purification.

Exceedance of the iron norm in the water may provoke allergic reactions and organic iron may be the cause of stomach ulcer and duodenal ulcer. High concentration of the iron in the water creates favorable conditions for the development of iron bacteria, especially in the warm water. Waste products of the iron bacteria are cancerogens. In this connection, the development of new and improvement of the available methods of iron extraction from the membrane blocks of water purification installations is urgent practical problem [3].

One of the important tasks in the process of purification is the control of pH level. At the value of pH> 4.5 ferrous iron is oxidized to ferric iron and precipitates in the form of hydroxide, the completeness of the oxidation increases with the increase of pH [4].

Aim of the study is the search of optimal ways of membrane block cleaning from the compounds of the ferric iron. It is worth taking into account ecological and economic effects, i. e., this method must be ecologically safe and economically accessible, that enables to use it in practice, increasing the term of service life of the membrane block of baromembrane installation for water purification.

Corrosive properties of food acids and characteristic features of their usage

Corrosive aggressivity depends on the presence of the corrosive-active organic acids in the system. The higher is the concentration of acid, the greater is its ability to dissolve the iron compounds. It was proved that the greatest corrosive losses of metal emerge if the concentration of the malic acid reaches the value of 0.5 %. [5]. That is why, proceeding from the analysis of scientific sources, the decision was made to use the aqueous solution of the food acid $C_4H_6O_5$ for the elimination from the surface of the membrane blocks one of the typical and main pollutants of water and, correspondingly, membranes of baromembrane installations – compound of ferric iron.

Acid $C_4H_6O_5$ is relatively safe, it does not refer to toxic or explosive substances and due to its dibasic and dual properties (features, characteristic both for acids and alcohol) does not require special storage conditions, cost efficient and has wide range of application in pharmacology, food and consumer goods industry, etc. [6].

According to the results of the research [7] it is known that the greatest corrosion behavior has hydrochloric acid and the least behavior – acetic acid. Corrosion rate of metals while using hydrochloric acid at the temperature of 293 K is seven times higher, and if the temperature reaches 353 K the corrosion rate increases 3 – 7 times. That is why, usage of the hydrochloric acid is rather dangerous and may cause the damage of the membrane, that makes its usage as the cleaner of the membrane blocks useless.

Also the decision was made to use aqueous solutions of the food acetic acid and citric acid. These acids are less active concerning the compounds of the ferric iron but are also safe from the point of view of the environment protection, possibility of utilization and prime cost of the substances. Experiment showed that citric acid has very weak corrosion properties and is practically inefficient for cleaning the membranes of baromembrane installations.

Experimental studies, using aqueous solutions of the food acids for the extraction of iron compounds

The solution of $FeCl_3 \cdot 6H_2O$ with the concentration of ions Fe^{3+} 10 g/l was used as the standardized test solution, 600 ml of the distilled water were added to 48.21 g of $FeCl_3 \cdot 6H_2O$. Solution was divided into three equal parts, the first part was brought to pH=7 by means of the solution NaOH (M=1 mole/l, ν=0.1784 mole) and remained in such state in the closed vessel for the observation.

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_3\downarrow + 3NaCl \quad (1)$$

Observations showed that the iron during one month remained in the form of the precipitation, i. e., ordinary water steeping of the membrane block is inefficient and inexpedient. In the same way the second part of the standardized test solution was brought to pH=7, i. e., to the formation of the precipitation, flokes of dark-orange color (Fig. 1).

Fig. 1. Precipitated compounds of Fe^{3+}, formation of flakes

After that the second portion was filtered and dried in the air till obtaining the constant mass. Further attempts to clean the filter paper from Fe^{3+} compounds by means of mechanical method showed that this method is also inefficient as part of the filtered precipitation remains at the filter material. That is, cleaning of the membrane block will not produce the desired result. Partially cleaned membrane will not function properly.

The third part of the solution was also brought to the value of pH=7 by means of the solution NaOH. Then it was divided into two equal parts, their calculated volume was 255 ml each. The solutions was allowed to stand in the measuring tube and the water above the precipitation was carefully poured. In each measuring tube the weight of Fe^{3+} ions was 1.67 g. 100 ml. of 9% aqueous food solution of $C_2H_4O_2$ acid was added to the first part. Ferric acetate (III) is formed, i. e., in real conditions in such a way we clean the membrane block from Fe^{3+}, allocating it into the separate compound.

$$Fe(OH)_3 + 3CH_3COOH \rightarrow (CH_3COO)_3Fe + 3H_2O \quad (2)$$

To the second part 100 ml. of 6% aqueous food solution of $C_4H_6O_5$ acid is added and iron malateis obtained:

$$2Fe(OH)_3 + 3HOOC{-}CH_2{-}CH(OH){-}COOH \rightarrow (HOOC{-}CH_2{-}CH(OH){-}COO)_3Fe_2 + 6H_2O \quad (3)$$

Our further task is to determine which solution of these acids is more efficient for cleaning the membrane of the reverse osmosis from the compounds of the ferric iron. For this purpose in certain time intervals (1, 2, 3 and 4 hours) from each solution samples are taken, these samples are analyzed for the content of iron on the calibration curve. The higher the content of iron is the more efficient the cleaning method is. According to the calibration graph balanced concentration of Fe^{3+} is found.

For the construction of the calibration graph measurement of the optical density of the studied solutions and determination of ferrum (III) content by means of photocolorimeter КФК-2 is carried out. For this purpose standard solution is prepared, 4.821 g of $FeCl_3 \cdot 6H_2O$ is diluted in 100 ml of the distilled water. Concentration of ferrum (III) ions in the standard solution is 10 g/l. Working solutions are prepared by means of adding the distilled water to the set amount of the standard solution. In measuring cylinders of 25 ml of the volume 0.0; 2.0; 4.0; 6.0; 8.0; 10.0 ml of the standard solution is measured. After adjusting the volumes by means of the distilled water to 10 ml, a series of working solution with ferrum (III) 0; 2; 4; 6; 8; 10 g in 1 l is obtained. In the process of photometric determination of Fe^{3+} ions content in the studied solutions it is expedient to make use of the green light filter with the wave-length λ= 540 nm and the cell with the thickness of the working layer 50 mm. Results of measurements are presented in Table 1.

Table 1

Results of measuring of the optical density of the solutions with different concentration of Fe^{3+} ions

Amount of the solution, V_n (ml) of Ferrum (III),	Concentration, C_n, (g/l) of Ferrum (III),	Optical density, D_n
2	2	0.23
4	4	0.37
6	6	0.49
8	8	0.61
10	10	0.7

Calibration curve is constructed according to the corresponding obtained results (Fig. 2).

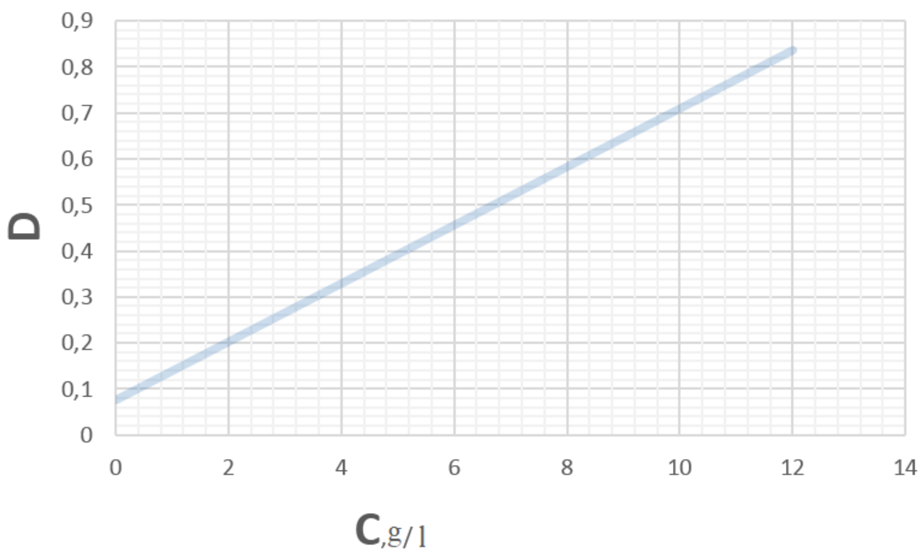

Fig. 2. Calibration curve of Fe^{3+} content

Obtained values of the optical density of ferric iron ions in the solutions with acetic (formula 2) and malic (formula 3) acids are summarized in the Table 2 and by means of the calibration curve, constructed above, corresponding concentrations of Fe^{3+} ions are found.

Table 2

Results of measurement of the optical density and Fe^{3+} ions concentration in the solutions with $C_2H_4O_2$ and $C_4H_6O_5$ acids

Time interval, hrs	Optical density (in the solution of acetic acid)	Concentration of Fe_{3+} in the solution of acetic acid, g/l	Optical density (in the solution of malic acid)	Concentration of Fe^{3+} in the solution of malic acid, g/l
1	∞	≈ 0	∞	≈0
2	0.05	0.01	0.18	1.6
3	0.17	1.55	0.38	4.6
4	0.32	3.8	0.45	5.8

Thus ,analyzing Table 2 the conclusion can be made that 6% of the dibasic acid $C_4H_6O_5$ is more efficient to fight the precipitations of the compound of the ferric iron on the membrane blocks of the reversed osmose installation. This method can be used in real conditions as the aqueous solution of the acid $C_4H_6O_5$ gives better results in the process of the short-term maceration and is cost -efficient and ecologically safe. In case of the corresponding dilution the used solution can be discharged in the municipal waste.

Conclusions

As it follows from the results of the experiment and study of the available research, usage of the malic acid for cleaning the membrane blocks nowadays is the most accessible and safe method of eliminating the iron compounds. Acid $C_4H_6O_5$ has certain advantages over other methods, more complex and ecologically dangerous cleaners, namely:

– it is ecologically safe, is not referred to toxic or explosive substances;

– it can be used at room temperature both in household and industrial baromembrane installations;

– it does not require special conditions of usage, storage and transport;

– it is financially efficient, not expensive;

– it has dual properties (properties inherent to acids and alcohols), that is why, it can be used for cleaning membranes not only from the compounds of iron but also from many other typical pollutants;

– it is able rather quickly to clean the membrane from the compounds of the iron, that reduces the terms of the membrane blocks regeneration;

– it is not aggressive, does not damage the structural elements of the membrane block of the installation for baromembrane purification of water.

Thus, usage of the malic acid nowadays is efficient, accessible and ecological method of cleaning the membranes of the installations of nano- filtration, ultrafiltration and reverse osmosis installations,.

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