https://doi.org/10.58805/kazutb.v.1.22-204

IRSTI 87.15.02

RESEARCH OF CHEMICAL PROCESSES OF WASTEWATER TREATMENT

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Treatment of waste water of industrial enterprises from heavy and toxic metal ions is carried out by traditional reagent method, sorption and membrane technologies. One of the simplest, cheapest, available and effective methods is sorption purification. The peculiarity of the sorption cleaning method is the property of selective absorption from multicomponent solutions and high cleaning efficiency. Treated wastewater can be used in the water supply system of technical circulation. *The main of the research work is to study* the pH of natural adsorbents in flowing and clean water solutions, particle sizes in suspensions, sedimentation rate and adsorption properties of natural adsorbents for sorption purification of industrial wastewater from toxic metal ions. natural minerals from Almaty region have high sorption properties, that is, they can be used for sorption treatment of industrial wastewater.

Keywords: wastewater, natural adsorbent, spectrophotometric study, sedimentation analysis, sedimentation rate, sorption treatment, natural minerals

ИССЛЕДОВАНИЕ ХИМИЧЕСКИХ ПРОЦЕССОВ ОЧИСТКИ СТОЧНЫХ ВОД

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Очистка сточных вод производственных предприятий от ионов тяжелых металлов проводится традиционно реагентным методом, сорбционными и мембранными технологиями. Одними из наиболее простых,
менее дорогостоящих, доступных и эффективных способов являются сорбционные методы очистки. Однако использование сорбционных технологий обезвреживания крупнотоннажных промышленных стоков
накладывают специфичные требования к используемым адсорбционно-активным материалам: они должны
быть полифункциональными для обеспечения очистки стоков и выбросов в широком диапазоне их состава
по технологии скорых фильтров. Очищенные стоки могут использоваться в системах технического оборотного водоснабжения. Достоинства сорбционной очистки явлются возможность избирательного поглощения
веществ из многокомпонентных растворов и высокая эффективность очистки. *Целью исследовательской*работы является изучение рН природных адсорбентов в сточных и чистых водных растворах, размеров
частиц в суспензиях, скорости седиментации и адсорбционных свойств природных адсорбентов для сорбционной очистки промышленных сточных вод от ионов тяжелых и токсичных металлов. Установлено что,
природные минералы Алматинской области обладают высокими сорбционными свойствами и могут быть
использованы для сорбционной очистки промышленных сточных вод.

Ключевые слова: сточные воды, природный адсорбент, спектрофотометрическое исследование, седиментационный анализ, скорость седиментации, сорбционная очистка, природные минералы.

АҒЫНДЫ СУЛАРДЫ ТАЗАЛАУДЫҢ ХИМИЯЛЫҚ ПРОЦЕСТЕРІН ЗЕРТТЕУ

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Өнеркәсіптік кәсіпорындардың ағынды суларын ауыр және улы металл иондарынан тазарту дәстүрлі реагенттік әдіспен, сорбциялық және мембраналық технологиялармен жүзеге асырылады. Қарапайым, арзан, қолжетімді және тиімді әдістердің бірі - сорбциялық тазарту болып келеді. Сорбциялық тазарту әдісінің ерекшелігі көпкомпонентті ерітінділерден іріктеп сіңіру қасиеті және тазарту эффективтілігі жоғары болып келеді. Сорбциялық технологиямен ірі тонналық өндірістік ағынды суларды залалсыздандыру үшін адсорбциялық - белсенді материалдарға бірқатар талаптар қойылады. Соның бірі - тез сүзгілеу технологиясы кезінде, олардың құрамы кең ауқымды, полифункцияналды болу керек. Сорбция әдісі ерітіндіден улы заттарды бөліп алып, өнделген ағынды су арқарай қолдануға жіберіледі. Тазартылған ағынды суларды техникалық айналымдағы сумен жабдықтау жүйесінде қолдануға болады. Зерттеу мақсаты - өндірістік ағынды суларды ауыр және улы метал иондарынан сорбциялық тазарту үшін табиғи адсорбенттердің ағынды және таза судағы ерітінділерінің рН мәнін, суспензиялардағы бөлшектердің өлшемдерін, бөлшектердің шөгу жылдамдығын және адсорбциялық қасиетін зерттеу болып табылады. Алматы облысынан шыққан табиғи минералдардың бентонит-монтмориллонит, қызыл бентонит, цеолит және диатомит сорбциялық қасиеті жоғары, яғни өндірістік ағынды суларды сорбциялық тазалау үшін қолдануға болатыны анықталды.

Түйінді сөздер: ағынды сулар, табиғи адсорбент, спектрофотометриялық зерттеу, седиментациялық талдау, шөгу жылдамдығы, сорбциялық тазарту, табиғи минералдар

Introduction. Decontamination of industrial wastewater from heavy and toxic metal ions is carried out by traditional reagent, sorption and membrane technologies [1-2]. One of the simple, cheap, affordable and highly effective methods is sorption purification. The composition of natural sorbents was previously determined by X-ray phase analysis method [3]. In the work under consideration, colloidal-chemical parameters for wastewater treatment were studied: pH value of solutions, particle sizes in suspensions, particle sedimentation rate [4].

Adsorbent - natural sorbents: lime water, diatomite (Ile), red bentonite (Mukre), bentonite-montmorillonite (Sredniy Tentek) and zeolite (Maytobe field) were taken to study the parameters of the wastewater system. The pH value of the wastewater was recorded before and after treatment with milk of lime and sorbents. The presence of a highly acidic environment (pH \approx 1) in the sewage solution before treatment is due to the high concentration of sulfate ions, because the composition changes according to the formation of insoluble sediments when treated with an alkaline reagent. During the treatment of wastewater with a natural sorbent, the concentration of such sulfate ions

was shown to decrease. A spectrophotometric study of the waste water and sorbent system was carried out in the research work. Using the spectrometric method, it was determined that the rate of sedimentation of sorbents in wastewater is equal to the maximum - 1.4 units for diatomite and the minimum value - 0.8 units for zeolite. The conclusion of the spectrophotometric research revealed that it is possible to choose the selected sorbents for wastewater treatment.

Sedimentation analysis of distilled and wastewater was carried out to determine the amount of particles in sorbent suspensions. According to the analysis results, it was found that the main size of bentonite-montmorillonite, diatomite and zeolite particles is close to each other. Here, most of the suspensions contain particles whose sizes vary from $2.5 \cdot 10^{-5}$ m to $4.5 \cdot 10^{-5}$ m. In this series of adsorbents, bentonite (Mukry) differs in terms of particle sizes, it contains particles with an average size of $15-17 \cdot 10^{-5}$ m. In addition, there are also the largest particles, the size of which reaches $60 \cdot 10^{-5}$ m. During the sedimentation analysis of these suspensions in wastewater, the amount of bentonite-montmorillonite and red bentonite particles decreases compared to pure water. For the first mineral,

the diameter in tap water is $1.5 \cdot 10^{-5}$ m (diameter in distilled water is $2.5 \cdot 10^{-5}$ m), for red bentonite the diameter is $10 \cdot 10^{-5}$ m (diameter in distilled water is $15-17 \cdot 10^{-5}$ m). The decrease in the particle size of the studied minerals is directly related to their self-dispersion due to the destruction of the layered structure under the influence of water molecules and ions in the wastewater.

Materials and methodology. Natural minerals of Almaty region were used to study the colloidalchemical parameters in the wastewater-sorbent system. Diatomaceous earth is a light gray powder. The density is 1.4 g/cm³. Red bentonite from Mukri is a brown or reddish clay. Density - 1.03 g/cm³. Bentonite montmorillonite dark gray mud (Middle Tentek). The density is 1.8 g/cm³. Zeolite is a dark brown powder (Maytobe). The density is 1.9 g/cm³ [5]. One of the most important characteristics of solutions is the pH value. In the study, indicators before and after the treatment of wastewater with milk of lime were determined. For untreated wastewater, the environment is equal to pH≈1, that is, it indicates a very acidic environment. This is because untreated wastewater has a high concentration of strong acid anions. After cleaning the wastewater containing sulfate ions with milk of lime, the pH value of the medium changed to 9.98, that is, it changed to an alkaline medium. Such a sharp change in the acidity of the environment is explained by the effect of the Ca(OH), reagent, as a result of which the acid anions in it bind with the Ca²⁺

ion and form an insoluble precipitate, that is, metal hydroxides, which determines the high pH value of the environment in waste water [6]. In the considered scientific work, the pH of wastewater was determined with natural sorbents. For all types of sorbents, pH values were approximately 1.3-1.6, which means that natural sorbents are not adsorbed by acid residue. At the same time, a spectrophotometric study of the wastewater and sorbent system was conducted.

Discussion and results. The sedimentation rate of sorbents in wastewater was determined using the spectrometric method. The sedimentation rate is one of the most important characteristics of wastewater treatment with sorbents. High turbidity of water after purification is a negative factor [7]. The time dependence graph of the optical density of the wastewater-sorbent system is shown (Figure 1). As can be seen from Figure 1, the optical density is also different for different suspensions of sorbents in wastewater. It can be seen that the optical density of lime water is lower compared to other sorbents. This is because a 5% solution of lime water is a slightly cloudy white solution. In the optical density curve, this adsorbent settles maximally in 400 seconds, but the density of the solution changes by only 0.4 units. This is due to the presence of milk of lime $(Ca(OH)_2)$ suspension particles, that is, it indicates the retention of the muddy form of the wastewater solution after treatment.

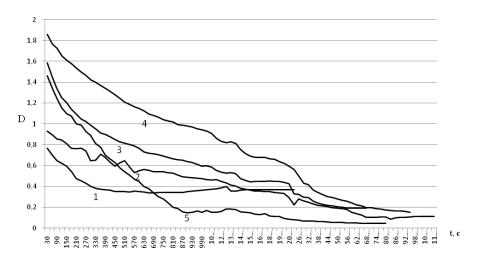


Figure 1 - Dependence of optical density of suspensions of sorbents in wastewater 1-lime water, 2-red bentonite, 3-bentonite montmorillonite, 4-zeolite, 5-diatomite

The initial and optical density values are close to red bentonite. Because the duration of the deposition is 2.5-3 hours. In general, the optical density of red bentonite decreases by 0.8 units. For bentonite-montmorillonite, zeolite and diatomite, optical density values are high in the initial part of the curves, that is, optical density value is greater than one (D>1). The reason for this is that at the beginning of the experiment, a muddy suspension is formed and the optical density increases. Montmorillonite has a long settling time like red bentonite, taking 2 hours for complete precipitation. Optical density decreases by 1.5 units.

Optical density for zeolite sorbent decreased by 1.8 units. In waste water, zeolite sorbent settles maximally after 2.5 hours. In general, it should be noted that the curves of bentonite-montmorillonite and zeolite lie

Diatomite

above other adsorbents, which means that the turbidity of the solution decreases slowly and, accordingly, the sedimentation rate of these suspension particles is low. The reason for this may depend on the size of the dispersed phase of the minerals.

The sedimentation rate of particles is high in diatomite suspension. The optical density of this mineral drops sharply from 1.48 to 0.18 within 15 minutes and completely settles after 2.5 hours. Compared to other suspensions, optical density in diatomite suspension is equal to 0.05, that is, it has the lowest value. A decrease in the curve in the graph indicates that the diatomite particles are larger in size than other sorbents. Using the results in the graph, the rate of decrease in optical density was calculated and listed in Table 1.

Adsorbent suspension	Optical density change rate
Lime milk	1.50•10–5
Red Bentonite	0.75•10–5
Montmorillonite	1.11•10–5
Zeolite	0.80•10–5

1.40 • 10 – 5

Table 1 – Rate of change in optical density in different suspensions

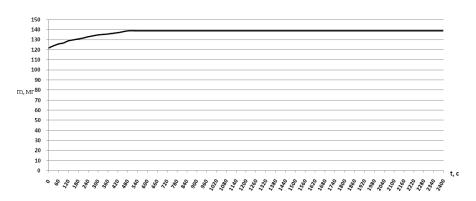


Figure 2 - Bentonite-montmorillonite sediment curve in distilled water

Table 1 shows that the rate of change in optical density for lime milk and diatomite is close, and in this series they are of maximum importance. In red bentonite and zeolite, the values of the rate of change determined by optical density are the lowest, the intermediate velocity of montmorillonite is characterized by a characteristic. Based on this data, diatomite is the fastest-growing sorbent compared to lime milk suspension. As noted above, in the

process of purification of lime with milk, the slurry of runoff water remains, which is a negative factor. Sedimentation analysis was carried out on each of them to determine the amount of particles in the sorbent suspensions. Figure 2 shows the deposition curve of bentonite-montmorillonite in distilled water. The sediment curve indicates dependence on the time-to-time change in the mass of the sediment.

m, mg	t, c	d, m 10–5	Q%
30	5	11	21.7
55	30	6.7	39.8
70	60	3.8	50.7
95	90	3	68.8
110	125	2.5	79.7
128	180	2.3	92.7
130	240	1.9	94.2
135	330	1.4	97.8
137	450	1.2	99.2

Table 2 - Data for calculating the size of fractions and percent of fractions

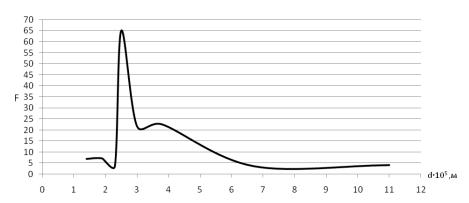


Figure 3 - Distribution curve of differential particle sizes in the system:

bentonite-montmorillonite - distilled water

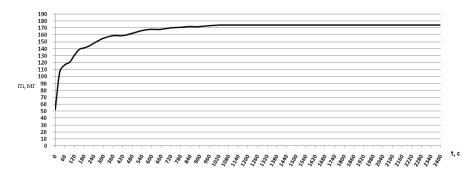


Figure 4 - Diatomite disobeyed water deposition curve

You can see in the graph that the changes in the sedientary mass in the initial time period are negligable. The size of the particles in this suspension (d, m) and the relative mass of the sediment [8] are calculated according to the methodology, the percentage of fractions with different diameter of particles (Q%) is given in Table 2 within m there are particles that change in diameter of particles. To get a visual representation

of the distribution of particle sizes in the system, a differential distribution curve is inserted, which is the diameter dependency of the mass distribution function $F=|\Delta Q/\Delta d|$, dQ/dd (in threshold value). In other words, from this graph you can determine the most likely amount of particles that will be in the polydisperse system, as well as the smallest and largest dimensions of the particles. The graph for bentonite-montmorillonite

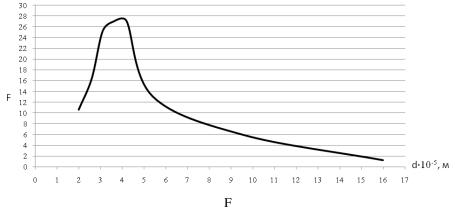
is shown in Figure 3.

As the graph shows, the most likely particle size for bentonite-montmorillonite is $2.5-3.0.0-10^{-5}$ m in diameter, the minimum particle size is $1.2-1.4\cdot10^{-5}$ m, And the maximum particle size is $11-10^{-5}$, figure 4, table 3, and figure 5 show the results of diatomite

suspension. will undergo significant changes. The particles calculated along the sediment curve are larger in size than bentonite-montmorillonite. You can see that most of the differential curve consists of parts 3.1– $4.5\cdot10^{-5}$ m in size, $1.4\cdot10^{-5}$ m in size, and $16\cdot10^{-5}$ m maximum (Fig. 5).

m, mg	t, c	d, m 10–5	Q%
13	5	16	7.5
22	30	9.59	12.7
65	65	5.4	37.7
92	150	4.2	53.4
120	210	3.6	69.7
130	450	3.1	75.5
140	570	2.6	81.3
151	810	2	87.7
172	930	1.4	99.5

Table 3 - Fraction sizing data and percent of fractions



igure 5 - The spread curve of the differential particle sizes in the system:

diatomite - distilled water

The data on bentonite is shown in figures 6, 7 and table 4. The initial cut of the curve in Figure 6 has little change in values, that is, at the beginning of the experiment the sediment forms very quickly, and the particle dimensions must be large, respectively, this forecast is confirmed by calculations (Table 4), according to which the dimensions of the specified particles reach $60 \cdot 10^{-5}$ m.

The possible size of the parts is $15-17\cdot10^{-5}$ m, the minimum is $5\cdot10^{-5}$ m. In this case, with spectrophotometric measurements, the dependence curve for bentonite should have decreased more

sharply than the diatomite curve, the reason for the gradual decrease in the optical density of bentonite and montmorillonite is the liophilic systems that are distributed in water. Montmorillonite is the main component of bentonite. They belong to hard-working silicates, which is explained by their easy swelling in the water. Since the structure of the layer consists of silicon-oxygen tetrahedrons and alumohydroxyl octaedres, and there is a weak connection between them, various ions enter the inter-package space, along with water molecules during swelling. The area of the specific surface of the montmorillonite is large

(600-800 m²/g) and is characterized by the ability to exchange 80-150 mmol eq/100 g of cations [9]. This will gradually dispersion, which will lead to a higher

silting of the solution, therefore, in the graph this is explained by a sharp decrease in optical density in the suspension of clays.

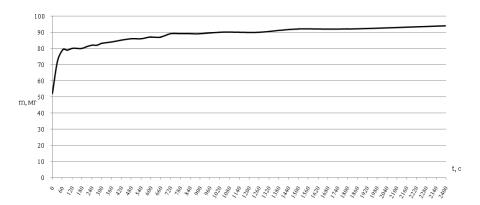


Figure 6 - Red Bentonite deposition curve in distiled water

Table 4 – Data for calculating the size of fractions and percentage of fractions

m, mg	t, c	d, m 10–5	Q%
12	5	60	13
20	30	35	21
30	150	20	32
49	330	15	52
79	510	13	85
82	630	11	88
85	690	9	91
87	720	7	94
90	840	5	98

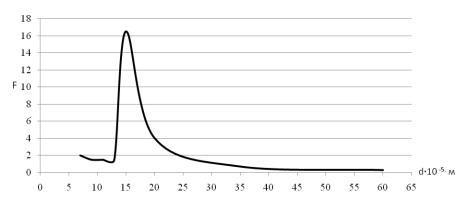


Figure 7 - The differential distribution curve of particle sizes in the system:

red bentonite - disobeyed water

Figures 8, 9 and Table 5 show the results of the sedimentation analysis of the ceolite, where you can also note

minor changes in the initial part of the curve (Figure 8), but as shown by the differential curve from this data, much of the system consists of particles measuring 3.0– $3.6 \cdot 10^{-5}$ m.

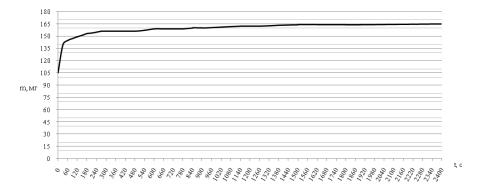


Figure 8 - Sediment curve in purified water of zeolite (Maitobe deposit)

Table 5 Table - Fraction sizing data and percent of fractions

m, mg	t, c	d, m 10-5	Q%
42	5	34	25,6
68	30	6,3	41,46
101	90	3,6	61,58
140	210	2,8	85,36
145	280	2,4	88,4
150	360	2,1	91,5
159	480	1,8	96,9
160	540	1,3	97,5
162	750	2,1	98,1

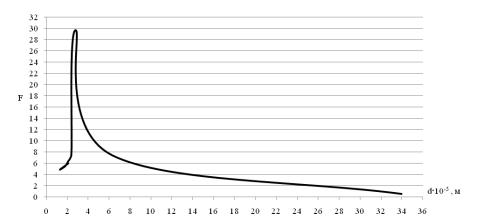


Figure 9 – The spread curve of differential particle sizes in the system:

ceolite-distilled water

After determining the amount of particles of natural sorbents presented above in disteeled water, particles of natural sorbents were detected in the wastewater. All the graphs and calculations were carried out in accordance with the previous practice.

As a result of the sedimentation study of natural sorbents in distilled and wastewater, the amount of suspense particles of bentonite - montmorillonite and bentonite is reduced compared to the pure water, the diameter of the first mineral in distilled water is 2.5·10⁻⁵ m. the diameter in runoff water decreased by 1.5·10⁻⁵ m. The diameter of red bentonite in disobeyed water was 15-17·10⁻⁵ m, and the diameter in runoff water was $10\cdot10^{-5}$ m. m decreased. The decrease in particle content of minerals may be related to the spontaneous violation of the complex structure of ions and water molecules containing wastewater. The structure of diatomite and cyolite minerals did not dispersion in the aquatic environment due to the strong structure, so in the sedimentation analysis, the amount of suspension particles of these minerals in distilled water and wastewater did not change much. Thus, the sedimentation analysis showed that suspensions of natural adsorbents belong to polysystems. This conclusion is explained by the fact that by spectrophotometric method, optical density

decreases slowly over time.

Conclusion. Natural minerals of Almaty region: bentonite - montmorillonite (Srednium Tentek deposit), red bentonite (Mukry deposit), zeolite (Maitobe deposit) and diatomite (Ili deposit) were extracted in the proposed study. For the treatment of natural minerals from industrial wastewater from heavy and toxic metal ions, the sorbbing properties were preliminarily studied using spectrophotometric and sedimentation methods. By spectrophotometric method, it was determined that the deposition rate of natural sorbent suspensions is equal to the maximum value for diatomite - 1.4 units and the minimum for the ceolitis - 0.8 units. The results of the spectrophotometric study revealed that these sorbents can be selected for wastewater treatment. Sedimentation analysis of distilled and wastewater was carried out to determine the amount of particles in sorbent suspensions. According to the results of the analysis, bentonite-montmorillonitis, diatomite and ceolite are close to each other in terms of the composition of the main particles.

It was determined that natural minerals from Almaty region have a high sorption properties, that is, industrial wastewater can be used for sorption treatment.

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