Determination of sorption properties of natural meliorants under static conditions

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Abstract. The presented research results are aimed at reducing the toxicity of wastewater containing heavy metals and ammonium ions on the environment, as well as their use as irrigation water for irrigation of industrial crops. The calculation of the volumetric static capacity for the given parameters, as well as the degree of extraction of pollution from the effluents, has been carried out. It was found that the highest percentage of absorption of heavy metals and ammonium ions after 48 hours of completed experiments is observed in zeolite with different fractions. After 12 hours of contact of the zeolite with poultry wastewater, it can be seen that 64.7% of total iron ions are absorbed, while activated carbon and gravel sand absorbed only 15.4%. Complex of activated carbon, gravel sand and zeolite 19.7%. After 48 hours of contact, the percentage of absorption of the zeolite decreased to 54.6%, and in the complex of activated carbon, gravel sand and zeolite to 3.1%, respectively, sorption was not observed in the activated carbon and gravel sand.

1. Introduction

In terms of chemical composition, the water resources of large cities in Russia can be classified as unsatisfactory [1]. A large amount of wastewater that has not at all passed the stage of preliminary treatment or is insufficiently treated is discharged into the water bodies of the regions. The largest contribution to the pollution of the water fund is made by housing and communal services, industrial, livestock and poultry enterprises [2–6].

Due to wastewater emissions, the state of surface waters, which do not meet sanitary standards, is of great concern. When performing chemical-analytical analysis of water samples, the content of toxic impurities, such as metal-containing impurities, nitrites, oil products, ammonium nitrogen, phenols, sulfates, exceeds [7–10].

The existing types of wastewater are of primary importance for the pollution of water resources, such as water bodies, rivers, lakes, etc. In the first place are the effluents entering water bodies from industrial enterprises, their volume causes no small damage [5, 6, 11]. From such industries, a large amount of various garbage gets into the rivers, as well as sewage containing impurities of toxic chemical elements [7, 8, 12].

There are many ways to purify waste water, such as sieving, primary sedimentation without reagents, filtration, sorption on activated carbon, ultrafiltration, ozonation, etc [11, 13, 14].
There are also many sorbents used for the purification and post-treatment of waste water. The most important property of any ameliorant is its sorption volumetric capacity.

2. Materials and methods
In this work, we propose to determine the sorption volumetric capacity of natural sorbents in the process of settling and filtering wastewater. The sorption process itself consists in the absorption of a solid or liquid substance by another substance [15–18]. Therefore, one of the main advantages of this method is the high degree of purification of various components and impurities from wastewater. Sorption is highly dependent on the physical properties of the adsorbents used due to their particle size, crystal structure, vibration wear and water resistance.

The sorption properties and absorption capacity of the ameliorants are also influenced by external factors - the time of contact of the sorbent with the test water, pH, pressure and volumetric capacity. Volumetric containers are of three types: absolute, dynamic and static. Static capacitance is greater than dynamic capacitance [1, 4].

All of the above parameters are necessary to determine the quality of the filter material in the process of purifying wastewater from heavy metal and ammonium ions. Zeolite flasks have a high cation exchange capacity. A distinctive feature of the sorbent is their high selectivity for large ions. The optimal time of contact of the sorbent with the dissolved substance makes it possible to reveal the most complete absorption of substances from the effluents. The adsorption effect is determined by a fixed volumetric capacity, which is determined by the number of ions of various impurities absorbed by a unit of mass or volume of the sorption material. There are three types of volumetric containers: full, dynamic and static [19–23]. The static capacity (stationary) is greater than the dynamic volumetric capacity (movable). When studying sorption materials, such as natural zeolite (tuff), activated carbon, gravel sand of various fractions, their absorbing properties to metals such as zinc, cadmium, copper, total iron, etc. were determined. Under static conditions, the most effective sorption material for the removal of various compounds from the studied wastewater was determined, as a result of which their characterizing data were obtained.

3. Results and discussions
The aim of the research is to determine the sorption properties of natural sorbents under static conditions. Before calculating the volumetric stationary container, it is necessary to add the investigated effluents to the adsorbent, stirring and during a specific period of time and the flask rotation speed of 1-2 revolutions per second, we separate the filtrate from the sorbent by settling and filtering.

For the amount of wastewater in a volume of 250 ml, a sorbent (zeolite, activated carbon, gravel sand) in a mass fraction of 60 grams was introduced at a time, when calculating, we obtain the equality of the balance.

\[ \text{COE} \cdot g + V \cdot C_{\text{equal}} = V \cdot C_{\text{ref}}, \]  

where: COE – at the given parameters, the static volumetric capacity, mg / g;
\( g \) – dry matter weight, g;
\( V \) – the amount of wastewater poured into the sorbent, l;
\( C_{\text{ref}} \) – initial concentration of impurities in polluted water mg / l;
\( C_{\text{equal}} \) – residual concentration of impurities after mixing the adsorbent and wastewater at different time intervals, mg / l

Calculation of volumetric static capacity for given parameters

\[ \text{COE} = \frac{(C_{\text{ref}} - C_{\text{equal}}) \cdot V}{g}, \]  

(2)
The degree of extraction of pollution from wastewater, %

$$E = \frac{C_{ref} - C_{equal}}{C_{ref}} \cdot 100,$$

(3)

After calculations, graphs of the dependence of the extraction of total iron ions by natural sorbents were built (Figure 1, 2, 3).

**Figure 1.** The degree of extraction of total iron, depending on the time of contact of waste water with zeolite of various fractions

**Figure 2.** The degree of extraction of total iron, depending on the time of contact of waste water with activated carbon and gravel sand
Figure 1 shows zeolite with fractions of 0.75, 1.0 and 4.0 mm as a sorbent, the degree of extraction of total iron within 20 minutes was 28.1%, in one hour 56.3%, within 12 hours 64.7%, after 24 hours the degree of total iron extraction was 59.7%, after 48 hours, 54.6% was adsorbed, there is little desorption.

From the graph, it can be seen where activated carbon and gravel sand were used as a sorbent when in contact with poultry wastewater for 20 minutes 1.4% of total iron is sorbed, for 1 hour 9.8%, for 12 and 24 hours the degree of extraction of total iron amounted to 15.4% after 48 hours, no sorption was observed.

Figure 3. The degree of extraction of total iron, depending on the time of contact of waste water with a complex of activated carbon, gravel sand and zeolite with a fraction of 4.0 mm

When used as a sorbent, I activated carbon, gravel sand and zeolite with a fraction of 4.0 mm upon contact with poultry wastewater for 20 minutes, 9.3% of total iron is sorbed, 15.2% for 1 hour, within 12 hours 19.7%, after 24 hours the total iron recovery was 16.3%, after 48 hours only 3.1% was adsorbed.

In the course of the experiments, the ability of various sorbents to absorb heavy metals and ammonium ions was studied. The results of the experiments on sorption properties showed that all sorbents used in the experiment absorb heavy metals and ammonium to one degree or another. Percentage data in effluents are given in Table 1.

The calculation of the static volumetric capacity, made according to formulas 2 and 3, showed that a greater percentage of absorption of heavy metals and ammonium ions after 48 hours of completed experiments is observed in zeolite with different fractions. After 12 hours of contact of the zeolite with poultry wastewater, it can be seen that it absorbed the total iron ions by 64.7%, as activated carbon and gravel sand only 15.4%. Complex of activated carbon, gravel sand and zeolite 19.7%. After 48 hours of contact, the percentage of absorption of the zeolite decreased to 54.6%, and in the complex of activated carbon, gravel sand and zeolite to 3.1%, respectively, sorption was not observed in the activated carbon and gravel sand. The calculation shows that the most optimal contact time of the sorbent is observed after 12 hours.

Under static conditions, it was found that sorbents absorb heavy metal and ammonium ions in various percentages, the results of which are summarized in Table 2.

It should be noted that after contact of sorbents with poultry wastewater for more than 12 hours, a slight desorption of the investigated substances occurs.
As a result of static processing of experimental data, the dependences were obtained, presented in the form of graphs, and characterizing the relationship between the concentration of the studied impurities and the time of contact of the zeolite with poultry wastewater (Figure 4, 5).

**Table 1.** Determination of absorption of complex sorbents as a percentage

| Name of the adsorbed ion | Absorption of heavy metals and ammonium,% |
|--------------------------|--------------------------------------------|
|                          | Zeolite fraction 0.75, 1.0, 4.0             |
|                          | 20 minutes | 1 hour | 12 hours | 24 hours | 48 hours |
| Iron total               | 28.1       | 56.3    | 64.7     | 59.7     | 54.6     |
| Iron II                  | 32         | 66.3    | 69.2     | 67.3     | 64.1     |
| Iron III                 | 35.5       | 67      | 75       | 72.7     | 70.3     |
| Chromium                 | 50         | 68.2    | 87.2     | 84.5     | 79.1     |
| Zinc                     | 51.5       | 80      | 87.6     | 86       | 77.6     |
| Copper                   | 53.7       | 68.5    | 71.4     | 62       | 57.1     |
| Cadmium                  | 18.75      | 50      | 56.25    | 53.1     | 46.8     |
| Ammonium                 | 39         | 67.6    | 82       | 80.9     | 74.2     |

| Activated carbon and gravel sand |
|----------------------------------|
| Iron total                       | 1.4       | 9.8    | 15.4    | No sorption | No sorption |
| Iron II                          | 2         | 9      | 12.1    | 10.2       | 4.5         |
| Iron III                         | 4         | 5.2    | 6.7     | 5.5        | 4.3         |
| Chromium                         | 9.1       | 9.1    | 18.1    | 9.1        | 9.1         |
| Zinc                             | No        | 15.3   | 23      | 7.7        | No sorption |
| Copper                           | No        | 14.2   | 20      | 11.4       | 2.8         |
| Cadmium                          | No        | 18.75  | 31.25   | 18.75      | 15.6        |
| Ammonium                         | 9.5       | 19     | 38.1    | 34.2       | 31.4        |

| Activated carbon, gravel sand and zeolite |
|-------------------------------------------|
| Iron total                                | 9.3       | 15.2   | 19.7    | 16.3       | 3.1         |
| Iron II                                  | 6.4       | 13.5   | 25.6    | 23.7       | 21.8        |
| Iron III                                 | 11.8      | 15.4   | 23.7    | 21.3       | 18.9        |
| Chromium                                 | 9         | 13.6   | 31.8    | 29         | 25.4        |
| Zinc                                     | 23        | 28.4   | 36.1    | 34.6       | 30          |
| Copper                                   | 28.5      | 42.8   | 48      | 47.1       | 44.8        |
| Cadmium                                  | 18.7      | 37.5   | 43.7    | 41.8       | 38.7        |
| Ammonium                                 | 19        | 30.4   | 47.6    | 43.8       | 40          |
Table 2. Determination of sorption of various sorbents in wastewater in relation to heavy metals and ammonium ions

| Name of substance | C_{init}, mg/l | Zeolite, Fraction 0.75, 1.0, 4.0 mm | Activated carbon and gravel sand | Activated gravel sand and zeolite | COE, eq/100 g |
|-------------------|---------------|-----------------------------------|---------------------------------|---------------------------------|--------------|
| Iron total        | 35.5          | 15.6                              | 15.3                            | 0.3                             | 0.001        |
| Iron II           | 15.6          | 15.3                              | 0.001                           | 14.6                            | 1.0          |
| Iron III          | 25.3          | 24.3                              | 0.004                           | 22.3                            | 3.0          |
| Chromium          | 1.1           | 1.0                               | 1.0                             | 0.0004                          | 0.1          |
| Zinc              | 1.3           | 1.3                               | 1.3                             | 0                               | 0.3          |
| Copper            | 3.5           | 3.5                               | 2.5                             | 1.0                             | 0.004        |
| Cadmium           | 1.6           | 1.6                               | 1.3                             | 0.3                             | 0.001        |
| Ammonium          | 10.5          | 9.5                               | 8.5                             | 2.0                             | 0.008        |
| Time of contact of wastewater with sorbent 20 minutes (0.3 hours) | 35.5 | 15.6 | 15.3 | 0.3 | 0.001 |
| Iron total        | 35.5          | 15.6                              | 15.3                            | 0.3                             | 0.001        |
| Iron II           | 15.6          | 15.3                              | 0.001                           | 14.6                            | 1.0          |
| Iron III          | 25.3          | 24.3                              | 0.004                           | 22.3                            | 3.0          |
| Chromium          | 1.1           | 1.0                               | 1.0                             | 0.0004                          | 0.1          |
| Zinc              | 1.3           | 1.3                               | 1.3                             | 0                               | 0.3          |
| Copper            | 3.5           | 3.5                               | 2.5                             | 1.0                             | 0.004        |
| Cadmium           | 1.6           | 1.6                               | 1.3                             | 0.3                             | 0.001        |
| Ammonium          | 10.5          | 9.5                               | 8.5                             | 2.0                             | 0.008        |
| Time of contact of wastewater with sorbent 1 hour | 35.5 | 15.6 | 15.3 | 0.3 | 0.001 |
| Iron total        | 35.5          | 15.6                              | 15.3                            | 0.3                             | 0.001        |
| Iron II           | 15.6          | 15.3                              | 0.001                           | 14.6                            | 1.0          |
| Iron III          | 25.3          | 24.3                              | 0.004                           | 22.3                            | 3.0          |
| Chromium          | 1.1           | 1.0                               | 1.0                             | 0.0004                          | 0.1          |
| Zinc              | 1.3           | 1.3                               | 1.3                             | 0                               | 0.3          |
| Copper            | 3.5           | 3.5                               | 2.5                             | 1.0                             | 0.004        |
| Cadmium           | 1.6           | 1.6                               | 1.3                             | 0.3                             | 0.001        |
| Ammonium          | 10.5          | 9.5                               | 8.5                             | 2.0                             | 0.008        |
| Time of contact of wastewater with sorbent 12 hours | 35.5 | 15.6 | 15.3 | 0.3 | 0.001 |
| Iron total        | 35.5          | 15.6                              | 15.3                            | 0.3                             | 0.001        |
| Iron II           | 15.6          | 15.3                              | 0.001                           | 14.6                            | 1.0          |
| Iron III          | 25.3          | 24.3                              | 0.004                           | 22.3                            | 3.0          |
| Chromium          | 1.1           | 1.0                               | 1.0                             | 0.0004                          | 0.1          |
| Zinc              | 1.3           | 1.3                               | 1.3                             | 0                               | 0.3          |
| Copper            | 3.5           | 3.5                               | 2.5                             | 1.0                             | 0.004        |
| Cadmium           | 1.6           | 1.6                               | 1.3                             | 0.3                             | 0.001        |
| Ammonium          | 10.5          | 9.5                               | 8.5                             | 2.0                             | 0.008        |
Table 2. Continuation

| Name of substance | C_{init}, mg/l | Zeolite, Fraction 0.75, 1.0, 40 mm | Activated carbon and gravel sand | Activated carbon, gravel sand and zeolite |
|-------------------|---------------|----------------------------------|----------------------------------|------------------------------------------|
|                   |               | C_{eq} mg/l | C_{eq} mg/l | COE, mg/l | C_{eq} mg/l | C_{eq} mg/l | C_{eq} mg/l | COE, mg/l | C_{eq} mg/l | C_{eq} mg/l | COE, mg/l |
| Iron total        |               | 35.5     | 14.3       | 21.2      | 0.09       | 30      | 5.5       | 0.46       | 29.7     | 5.8       | 0.02       |
| Iron II           |               | 15.6     | 5.1        | 10.5      | 0.043      | 14.0    | 1.6       | 0.006      | 11.9     | 3.7       | 0.015      |
| Iron III          |               | 25.3     | 6.9        | 18.4      | 0.07       | 23.9    | 1.1       | 0.006      | 19.9     | 5.4       | 0.022      |
| Chromium          |               | 1.1      | 0.17       | 0.93      | 0.003      | 1.0     | 0.1       | 0.0004     | 0.78     | 0.32      | 0.0013     |
| Zinc              |               | 1.3      | 0.17       | 1.13      | 0.005      | 1.2     | 0.1       | 0.0004     | 0.85     | 0.45      | 0.0018     |
| Copper            |               | 3.5      | 1.3        | 2.2       | 0.009      | 3.1     | 0.4       | 0.001      | 1.85     | 1.65      | 0.006      |
| Cadmium           |               | 1.6      | 0.75       | 0.85      | 0.0035     | 1.2     | 0.4       | 0.001      | 0.93     | 0.67      | 0.0027     |
| Ammonium          |               | 10.5     | 2.0        | 8.5       | 0.035      | 6.9     | 3.6       | 0.015      | 5.9      | 4.6       | 0.019      |

Time of contact of wastewater with sorbent 24 hours

| Iron total        |               | 35.5     | 16.1       | 19.4      | 0.08       | 30      | 5.5       | 0.46       | 31.4     | 4.1       | 0.017      |
| Iron II           |               | 15.6     | 5.6        | 10        | 0.041      | 14.9    | 0.7       | 0.003      | 12.2     | 3.4       | 0.014      |
| Iron III          |               | 25.3     | 7.5        | 17.8      | 0.074      | 24.2    | 1.1       | 0.004      | 20.5     | 4.8       | 0.02       |
| Chromium          |               | 1.1      | 0.23       | 0.87      | 0.003      | 1.0     | 0.1       | 0.0004     | 0.82     | 0.28      | 0.0011     |
| Zinc              |               | 1.3      | 0.29       | 1.01      | 0.004      | 1.3     | 0.0       | No         | 0.91     | 0.39      | 0.0016     |
| Copper            |               | 3.5      | 1.5        | 2.0       | 0.008      | 3.4     | 0.1       | 0.0004     | 1.93     | 1.57      | 0.0065     |
| Cadmium           |               | 1.6      | 0.85       | 0.75      | 0.0031     | 1.35    | 0.25      | 0.001      | 0.98     | 0.62      | 0.0025     |
| Ammonium          |               | 10.5     | 2.7        | 7.8       | 0.032      | 7.2     | 3.3       | 0.013      | 6.3      | 4.2       | 0.017      |

Time of contact of wastewater with sorbent 48 hours

Figure 4. Efficiency of zinc removal from poultry effluents, depending on the time of contact with zeolite
Figure 5. The efficiency of removing chromium from poultry effluents, depending on the time of contact with zeolite

4. Conclusions
The maximum absorption effect in the study of various sorbents under static conditions in relation to heavy metals and ammonium ion was obtained using natural zeolite, which ensures the removal of at least 50% of impurities from poultry wastewater, in contrast to sorbents such as activated carbon and gravel sand. Based on the research, the calculation of the sorption volumetric capacity of natural sorbents in the process of settling and filtering wastewater, as well as the degree of extraction of contaminants.

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