Effect of adsorption processes on oil-containing water purification by flocculation method

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Abstract. The results of the study of the processes of adsorption of cationic flocculants of the "Praestol" brand on sorbents obtained by non-chemical processing of clays of the Astrakhan region, the Volga deposit are presented. The adsorption models of Langmuir, Freundlich, and Temkin were used to describe experimental adsorption isotherms. The parameters of the intensity and efficiency of the sorption process are calculated. A comparative analysis of the obtained constants corresponding to these models is carried out and the most preferred model is determined, taking into account the coefficient of determination. It is established that the Freundlich model is most preferable for adsorption in the cationic flocculant – clay system, which allows us to confidently assume that the surface of the natural materials under consideration contains a large number of energetically heterogeneous active centers and is heterogeneous. The results of the analysis of the adsorption of flocculants on clays showed that this process improves flocculation. The bigger value of parameter of intensity of n from Freundlich's equation for Praestol 853BC flocculant, confirms a greater influence of sorption on flocculating effect that it is connected with formation of the strong high-viscosity sewed structures on a surface of a firm phase. Experiments on the purification of water from oil by test flocculation were also delivered and the degree of purification efficiency was calculated.

1. Introduction
Oil refining enterprises are considered to be one of the most powerful sources of water pollution. In the literature there is a large number of developments devoted to the treatment of natural and wastewater [1]. However, despite this, the problem cannot be considered solved. The current environmental situation dictates the need to improve existing and develop new technologies and methods of water purification for various purposes.

One of the ways to intensify existing technologies is the use of high-molecular organic flocculants, among which polyacrylamide flocculants are the most common and universal. A more extensive introduction and widespread use of these substances could not only increase the productivity and throughput of treatment facilities, but also increase the reliability and stabilize their operation under extreme loads [2].

The choice of flocculant for each specific case of water treatment is quite complex and requires additional research. This task will be facilitated by knowledge of the physicochemical basis, which will serve as the basis for the development of effective methods of water purification [3].

As is known, flocculation of contaminants present in waste water occurs in two stages: adsorption of flocculant on particles and formation of particle aggregates [4]. Sorption methods of purification, using natural materials as sorbents, are now common in industry [5].
The purpose of the presented study is to study the process of adsorption of cationic flocculants on natural minerals of the Astrakhan region, and to assess the effect of sorption on the treatment of oily waste water by flocculation.

Cationic flocculants, the Praestol brand, were taken as the subject of the study. These substances are organic, synthetic, high molecular weight compounds based on polyacrylamide and are copolymers of acrylamide with increasing fractions of cationic comonomers.

2. Materials and methods
The study of the processes of adsorption of flocculants on the clays of the Astrakhan region was carried out under static conditions. To obtain the sorbent, natural raw materials were crushed in ball mills, then fractions with a fixed particle size were sifted out on vibrating screens, washed in water to free them from soluble components and dried at a temperature of 102–120°C to a constant mass. Model solutions of cationic flocculants of the "Praestol" brand were used. The content of the latter before and after adsorption was determined by viscosimetry taking into account the background [6].

The sorbed amount of the substance \( Q (g/g) \) calculated by the formula (1):

\[
Q = \frac{(C_0 - C_\tau) \cdot V}{m} \cdot 1000
\]  

(1)

Where \( C_0 \) is the initial concentration of flocculant in solution, g/dm\(^3\); \( C_\tau \) is the concentration of flocculant in solution at time \( \tau \), g/dm\(^3\); \( V \) – solution volume, dm\(^3\); \( m \) – mass of sorbent, g [7].

In order to assess the efficiency of using the natural resources of the Astrakhan region as sorbents for purifying water from oil products using flocculants, preliminary experiments were conducted. Model wastewater was prepared in such a way that the concentration of petroleum products was more than 100 times higher than the MPC for drinking water. Purification efficiency is calculated by formula (2):

\[
S = \frac{C_0 - C}{C_0} \cdot 100\
\]  

(2)

Where \( S \) – the cleaning efficiency, %; \( C_0 \) – the initial concentration, g/dm\(^3\); \( C \) – the residual concentration, g/dm\(^3\).

Flocculation was studied on model systems using clays. The suspension was prepared such that the concentration of the dispersed phase in the suspension was 1%. To describe and estimate the flocculating effect, the relative parameter \( D \) was used, which was calculated by the formula (3):

\[
D = \frac{A_0 - A}{A}
\]  

(3)

Where \( A_0 \) and \( A \) - respectively the optical density of water (determined by a turbidimetric method) in the absence and presence of a flocculant.

3. Results
As a result of experimental research and theoretical calculations, isotherms of sorption processes of cationic flocculants on natural sorbents of the Astrakhan region were obtained (figure 1).

Analysis of experimental data shows that the equilibrium sorption capacity of clay with respect to flocculants is approximately the same and is 0.11 and 0.12 g/g for Praestol 650 BC and Praestol 853 BC, respectively.
The adsorption equilibrium data were processed according to the equations for the Freundlich, Langmuir, and Temkin isotherms [8], and the results are presented in table 1.

Table 1. Flocculant adsorption intensity and efficiency parameters obtained in the Langmuir, Freundlich and Temkin models.

| Type of isotherm | Praestol 853 BC | Praestol 650 BC |
|------------------|----------------|-----------------|
| **Freundlich**   | n = 2.61       | n = 2.5         |
| **Langmuir**     | $K_L = 2.46 \text{ dm}^3/\text{g}$ | $K_L = 2.36 \text{ dm}^3/\text{g}$ |
| **Temkin**       | $K_T = 73.7$  | $K_T = 85.9$   |
| Efficiency       | $K_F = 12.8$  | $K_F = 15.6$    |
| $Q_e$  | 0.12 g/g  | 0.11 g/g       |
| $R^2$           | 0.9866       | 0.9768          |

The calculated flocculating effect values for the flocculants Praestol 853 BC and Praestol 650 BC are shown in table 2.

Table 2. Flocculating effect for the flocculant Praestol 853 BC and Praestol 650 BC.

| $\tau$, min | 1 | 2 | 3 | 5 | 1 | 2 | 3 | 5 |
|-------------|---|---|---|---|---|---|---|---|
|             | Praestol 650 BC | Praestol 853 BC | Praestol 650 BC | Praestol 853 BC | Praestol 650 BC | Praestol 853 BC | Praestol 650 BC | Praestol 853 BC |
| 0           | 0.91 | 1 | 0.96 | 1.04 | 0.11 | 0.08 | 0.05 | 0.04 |
| 5           | 1.34 | 7.47 | 8.04 | 7.11 | 1.24 | 10.76 | 6.41 | 18.23 |
| 10          | 1.73 | 7.96 | 8.2 | 7.24 | 1.48 | 12.16 | 7 | 20.43 |
| 20          | 1.93 | 8.04 | 8.32 | 7.6 | 1.7 | 13.56 | 7.17 | 22.62 |
| 30          | 2.25 | 8.8 | 9.56 | 8.68 | 2.02 | 15.57 | 9.03 | 28.7 |

4. Discussion

A comparative analysis of Table 1 data on constants and determination coefficients ($R^2$) has established that both the equation for an inhomogeneous surface (Freundlich, Temkin) and the Langmuir equation for a homogeneous surface can be formally applied to describe the adsorption
equilibrium of flocculants on clay. However, the Freundlich isotherm is most preferred. The Freundlich model gives a maximum value of $R^2$. This further indicates that there are many active centers with different energies on the surface, that is, it satisfies the boundary conditions for the applicability of the Freundlich model with a heterogeneous coating [9].

Note that the values of the parameter $n$, which indicates the intensity of the sorbent – sorbate interaction, are higher for the flocculant Praestol 853BC, which is associated with the formation of strong high-viscosity cross-linked structures on the surface of the solid phase. The obtained value of the constant $K_F$ in the Freundlich equation (characterizing the adsorption capacity) for the flocculant Praestol 650BC is higher, which indicates a greater sorption value [10-13].

Analyzing the results of calculations of the efficiency of water purification from oil by the trial flocculation method, it seems possible to draw conclusions that the Praestol flocculant 853BC more effective for oil purification. Efficiency of purification is 81.3% with minimal addition of flocculant with volume of 1 cm$^3$ per 100 cm$^3$ of model solution. The efficiency for the Praestol 650BC flocculant was 75.4%, with a minimum volume.

Analysis of table 2 shows that the highest deposition rate is observed using the Praestol 853 BC flocculant. The flocculating effect is higher for the Praestol 853 BC flocculant. It can also be concluded that the suspension of Praestol 853 BC is most effectively clarified, although the process is slower than the flocculation of Praestol 650 BC. This effect can be explained by the formation of higher viscosity structures of polymer macromolecules, since the molecular weight of Praestol 853 BC is greater, all of which together intensify flocculating properties.

5. Conclusion

When describing the adsorption equilibrium of flocculants on the natural resources of the Astrakhan Region, it is preferable to use the Freundlich isotherm, which indicates the presence of a large number of active centers and their exponential distribution on the surface of sorbents.

Analysis of adsorption isotherms using the Freundlich and Langmuir models, in general, allows us to characterize clays as a multiporous material. Presumably, the main contribution to the implementation of the adsorption mechanism in this case is made by the process of internal diffusion.

The obtained parameters of the Temkin adsorption model confirm the main characteristics of the Freundlich model and indicate a uniformly inhomogeneous surface of the sorbent based on clays.

Preliminary experiments on water purification from oil by flocculation using clay allowed us to evaluate the effectiveness of water purification. It was found that both analyzed flocculants are quite effective. The Praestol 853BC flocculant has a slightly higher percentage of cleaning efficiency compared to the Praestol 650BC flocculant.

Adsorption affects both flocculation processes and the flocculating effect. Given all of the above, this study could provide a chemical basis for addressing environmental safety issues.

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