Glycerol modifier influence on interfacial activity of bentonite during the adsorption of o-toluidine

A V Kosarev1*, E I Tikhomirova1, N A Politaeva2 and A L Podolsky1

1Gagarin State Technical University of Saratov, School of Urbanistics, Civil Engineering and Architecture, Polytechnicheskaya, 177, Saratov, 410054, Russian Federation
2Peter the Great St. Petersburg Polytechnic University, Higher School of Biotechnology and Food Technology, Polytechnicheskaya, 29, St.-Petersburg, 195251, Russian Federation

* Corresponding author: aleteia@inbox.ru

Abstract. This paper is devoted to the study of changes in the surface activity of systems containing unmodified bentonite and bentonite modified with glycerol additives upon adsorption of o-toluidine. A relationship between surface activity and the value of o-toluidine adsorption on modified aluminosilicate was obtained. It is shown that the presence of a modifier-glycerol in the adsorption system enhances the process of lowering the surface tension.

1. Adsorption activity of modified aluminosilicates

The purification of industrial wastewater from organic compounds plays an important role for applied ecology today. Meanwhile, models of the relationship between the structural and adsorption characteristics of aluminosilicate systems under conditions of dynamic adsorption have not been sufficiently developed. Clay materials are one of the most effective types of adsorbents. It should be noted montmorillonite, which is the main component of natural bentonite. This was established in [1] the influence of the structural factor in the modification of montmorillonite by intercalation, which leads to an increase in the proportion of active adsorption centers on the surface of the aluminosilicate. It is also shown that this leads to an increase in the efficiency of adsorption of heavy metals on them. The authors [2] showed that aluminosilicates adsorption activity is determined by the structural characteristics of the system: the interplanar distance, the distribution of the adsorption centers along the surface of the adsorbent, the diameter of the adsorptive molecule. In [3] it was found that the nature of formaldehyde adsorption on aluminosilicate adsorbents depends on the type of modification of the adsorbent: acid modifiers change the specific surface of the adsorbent more efficiently than the main ones.

The authors of [4] showed that the processes of adsorption of zinc ions from solutions on natural and modified montmorillonites can be described using Langmuir and S-shaped isotherms, the shape of which is determined by both the surface properties of the sorbent and the forms of zinc ions in aqueous solutions. In [5] it was established that cationic dyes molecules can aggregate with each other as a result of aluminosilicates surface adsorption, which leads to an increase in the efficiency of their extraction from water. The authors [6] showed that for the adsorption of methylene blue and crystal violet at low values of the adsorption capacity the endothermic effect prevails, and at high values the exothermic effect prevails.
The authors [7-8] note that the adsorption of cationic forms of dyes on aluminosilicates has a monomolecular mechanism that follows the Langmuir adsorption isotherm and is an endothermic process, during which adsorbent-adsorbate layers with low orderliness are formed. A technology for purifying water from the Orange II dye was proposed in [9]. Processes of preliminary extraction of cationic surfactants from waste and the subsequent use of organomodified bentonite were combined in this technology. It was shown in [10] that anionic dyes are also effectively removed from water using aluminosilicates, modified hescamethylene diamine. The authors [11] note that clinoptilolite can be a very effective adsorbent for removing organic dyes, such as safranin T, from wastewater.

Adsorption mechanism obeys the Langmuir isotherm in this case. At the same time, the adsorption of toduidine blue on a given zeolite is described by a second-order kinetics model and obeys isotherms of both Langmuir and Freundlich [12]. The kinetics of main green and basic violet ions adsorption on the surface of montmorillonite was simulated using the fractal approach. Electrostatic interactions are not dominant in the interaction "zeolite - the main dye" [14]. The authors of [15] showed that montmorillonite, modified in an alkaline medium with polyethyleneimine, is associated with it through electrostatic interactions. The mechanism of modifying aluminosilicates with the addition of surface-active polymer modifiers is discussed in article [16]. Three types of composite materials are distinguished in depending on the structure of the components and the conditions of synthesis. traditional microcomposite is formed in the case when the modifier molecules do not penetrate into the layer structure of the aluminosilicate. The second modification variant corresponds to the intercalated composite, corresponds to the case when the modifier molecules penetrate into the interlayer space of the aluminosilicate and cause an increase in this distance and changing the adsorption activity of the system. The third variant of the modification, exfoliated nanocomposite, corresponds to the case when the modifier molecules completely separate the particles of aluminosilicate, so that they completely lose their orderliness. [17,18]. It was shown in [19] the adsorption of cationic dyes on aluminosilicate modified by cationic surfactants is due to the hydrophobic interaction of the adsorbate with the modified surface, as well as due to ion exchange.

2. Adsorption process modeling

The ratio between surface tension coefficient $\sigma$ and the adsorption characteristics of the adsorbate associated with the aluminosilicate is given by the Gibbs equation:

$$\frac{\Gamma_mRT}{C} = -\frac{\partial \sigma}{\partial C} \Gamma_0$$

where $\Gamma_0$ = the value of adsorption of o-toluidine on the modified aluminosilicate; $C$ is the equilibrium concentration of the adsorbive in the aqueous macrophase of the solution; R is the universal gas constant; T-temperature. The ratio $(-\partial \sigma / \partial C)$ characterizes the surface activity of the adsorbing substance. For bentonite modified with non-ionic modifier additives, the equation (1) is:

$$\frac{\Gamma_mRT}{C} = -\frac{\partial \sigma}{\partial C}$$

The surface tension of a system containing modified aluminosilicate $\sigma_m$ is related to the surface tension $\sigma$ of a system containing unmodified aluminosilicate by the ratio

$$\sigma_m = k\sigma$$

where k is the coefficient, showing how many times the adsorption of this component on the modified adsorbent is higher than on the non-modified one:

$$k = \frac{\Gamma_mRT}{\Gamma_0RT}$$

where $\Gamma_mRT$ and $\Gamma_0RT$ = values of the limiting absorption capacity in relation to this adsorbate modified and non-modified aluminosilicates respectively. From equations (1) and (2) taking into account (3), the:

$$\left(\Gamma_m + \Gamma_0RT\right)\frac{RT}{C} = -\frac{\partial \sigma}{\partial C}(1+k)$$

It follows that the amount of surface activity caused by the modification of aluminosilicate can be found in the following way:
3. Experiment results
We have experimentally studied the adsorption of o-toluidine on pure bentonite, and on the bentonite, modified by glycerol additives. Laboratory investigations are performed on the basis of the scientific and educational center "Industrial ecology" of Gagarin State Technical University of Saratov with the use of the verified test and auxiliary equipment.

Figure 1. Change of surface activity $(-\partial\sigma/\partial c)$ on bentonite, modified glycerol (curve 1) and non-modified bentonite (curve 2) from the equilibrium concentration of o-toluidine in solution.

Experimental determination of the amount of adsorption capacity is based on determination of residual concentration of o-toluidine in the aqueous phase of the solution containing adsorbent. We had an experiment to determine this value. We dissolved 1.5 g of 2-naphthene-3,6-disulfonic acid sodium salt in 50 ml of distilled water. Then we added the obtained solution Na2CO3 to the resulting system and diluted with water to the volume of 100 ml. We mixed 1 ml of the solution with 1 ml 2 N hydrochloric acid and added 1 ml of 0.25% solution NaNO2 for the reaction of diazotization. We poured this solution in 15 minutes with 10 ml of 1 M solution Na2CO3 and 0.5 ml of reagent solution, and then diluted with water to a volume of 25 ml. After 1 h we photometric the resulting solution on a two-beam scanning UV-type Spectrophotometer «Promekolab» PE-6100 UV at a wavelength of 485 nm [20].

Increase of the size $(-\partial\sigma/\partial c)$ at increasing of concentration o-toluidine is caused by decrease of a superficial tension at adsorption (Fig. 1). The presence of the modifier-glycerol leads to an increase in the interlayer distance in the structure of adsorbent, as well as the of micro-environment polarity reduction of the molecules o-toluidine. It is strengthens the process of lowering the surface tension.

This work is topical for consideration of industrial ecology problems on improvement of adsorption purification of sewage from organic compounds by modification of aluminosilicate adsorbents.

4. Conclusions
The work shows that the presence of the modifier-glycerol leads to increase in the dependence of the surface activity of the system $(-\partial\sigma/\partial c)$ from the concentration of o-toluidine in the solution. It is can be explained by the fact that presence of the modifier-glycerol leads to an increase in the interlayer distance in the structure of adsorbent, as well as the of micro-environment polarity reduction of the molecules o-toluidine. It is strengthens the process of lowering the surface tension.

The given work is the result of carrying out of research work within the framework of grant for winners of competitive selection of the projects executed by scientific collectives of research centers and (or) scientific laboratories of educational Organizations of higher education (state task of the Ministry of Education and Science of the Russian Federation, project 5.3922.2017/PCh).
References

[1] Yurchenko V V, Sviridov A V, Sviridov V V, Nikiforov A F, Pryanichnikov S V 2017 Sorption and chromatographic processes 17 p 506
[2] Ivanova E S, Gavronskaya Yu Yu, Stozharov V M, Pak V N 2014 J. general chem 84 p 185
[3] Nazimova L A, Strelnikova O Yu, Khodosova N A, Belchinskaya L I, Roessner F 2014 Sorption and chromatographic processes 14 p 185
[4] Ganebnykh E V, Sviridov A V, Maltsev G I 2015 Chemistry for sustainable development interes. 1 p 89
[5] Miyamoto N, Kawai R 2000 Applied Clay Science 16 p 161
[6] Rytwo G, Ruiz-Hitzky E 2003 J. of Thermal Analysis and Calorimetry 71 p 751
[7] Insuwan W, Rangstriwatananon K 2014 J.of Porous Mater. 21 p 345
[8] Khenifi A, Boubeka Z, Sekrane F 2007 Adsorption 13 p 149
[9] L Zhu 2008 J. Ma Chem. Eng. J. 139 p 503
[10] Alver E, Metin A U 2012 Chemical Engineering J. 200 p 59
[11] Qiu M, Qian Ch, Xub J, Wu J, Wang G 2009 Desalination 243 p 286
[12] Alpat S K, Ozbayrak O, Alpat S, Akçay H 2008 J. of Hazardous Materials 151 p 213
[13] Wang C C, Jiang C L, Hsu T C, Lee C K 2004 J. Colloid Interf. Sci. 273 p 80
[14] Hu Q H, Qiao S Z, Haghseresht F, Wilson M A, Lu G Q 2006 Ind. Eng. Chem. Res. 45 p 733
[15] Pshinko G N, Puzynnaya L N, Kosorukov A A, Goncharuk V V 2010 Radiochem. 52 p 291
[16] Chvalun S N, Novokshonova L A, Korobko A P, Brevnov P N 2008 Russian Chem. J. LII p 52
[17] Hussain F, Hujjati M, Okamoto M, Gorga R E 2006 J. of Composite Material. 40 p 1512
[18] Alix S, Follain N, Tenn N, Alexandre B 2012 J. Phys. Chem. 116 p 4937
[19] Tarasevich Y I, Trifonova M Y, Bondarenko S V, Dolenko S A 2010 Colloid J. 72 p 565
[20] Kosarev A V, Atamanova O V, Tikhomirova E I, Istrashkina M V 2018 Water and ecology: problems and solutions 3(75) p 24