CHEMICAL ENGINEERING TRANSACTIONS
VOL. 102, 2023
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Laura Piazza, Mauro Moresi, Francesco Donsì

ISBN 979-12-81206-01-4; **ISSN** 2283-9216
DOI: 10.3303/CET23102059

Some Aspects of Mathematical Modeling of the Geometric Structure of Porous Vermiculite Adsorbents used in the Refining of Vegetable Oils

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Currently there are high requirements for the quality of vegetable oils and fats, which is ensured only by a highly efficient technological cleaning process. Adsorption refining has become widespread, since the resulting products not only satisfy consumer demand, but also allow the removal of oxidation products, free radicals and other carcinogenic impurities from the oil. For such oil purification, it is necessary to select not only optimal oil refining modes, but also using effective adsorbents and bleach lands.
This article describes some aspects of mathematical modeling of the geometric structure of porous adsorbents, since one of the main tasks of porous adsorbents production is creation of high porosity, which is also characterized by the uniformity of the pore distribution over the volume of the layer. Ensuring optimal modes of porization processes and achieving the necessary geometric characteristics of the adsorption layer requires an understanding of the features of the layer structure formation and a theoretical description of this complex process, as well as the results of studies on the purification of cottonseed oil with expanded vermiculite from the Kulantau deposit and the characteristics of a new adsorbent for vegetable oils are presented.
Practical application development of theoretical aspects of the vermiculite adsorbent porosity effect on the quality of refined vegetable oil.
Key words: vegetable oil, adsorbent, Kulantau, vermiculite, porosity, geometric structure, refining.

1 Introduction

Currently there are high requirements for the quality of vegetable oils and fats, which is ensured only by a highly efficient technological cleaning process. Edible vegetable oils must be subjected to a full cycle of refining in order to remove substances harmful to the body, improve quality, improve organoleptic characteristics, as well as ensure resistance to oxidation. In the world practice, this type of adsorption refining has become widespread, since the resulting products not only satisfy consumer demand, but also allow the removal of oxidation, free radicals and other carcinogenic impurities from the oil. For such oil purification, it is necessary to select not only the optimal oil refining modes, but also to use effective adsorbents and bleaching clay. (Arutyunyan et al., 2015).
Vermiculite from the Kulantaus deposit was used in the work. Industrial tests of expanded Kulantaus vermiculite have shown the possibility of its effective use for vegetable oil adsorption cleaning instead of expensive imported bleaching clays.
This article presents the results of research on the purification of vegetable oil with expanded vermiculite, the characteristics of a new adsorbent for vegetable oils, describes some aspects of mathematical modeling of the geometric structure of porous adsorbents, since one of the main tasks in the production of porous adsorbents is creating high porosity. Ensuring optimal modes of porization processes and achieving the necessary geometric characteristics of the adsorption layer requires an understanding of the features of the formation of the layer structure and a theoretical description of this complex process. The quality of the resulting products depends on adsorbed vegetable oil.

Paper Received: 14 March 2023; Revised: 20 May 2023; Accepted: 7 August 2023
Please cite this article as: Kaldybekova Z.B., Syrmanova K.K., Bayzhanova S.B., Agabekova A.B., Kurmasheva M.B., Bekbol M.Z., 2023, Some Aspects of Mathematical Modeling of the Geometric Structure of Porous Vermiculite Adsorbents Used in the Refining of Vegetable Oils, Chemical Engineering Transactions, 102, 349-354 DOI:10.3303/CET23102059

2 Materials and Methods

Cottonseed oil was used in the work (Bezdenezhnykh et al., 2017). Expanded vermiculite of the Kulantau deposit was used as an adsorbent in the work (Kaldybekova et al., 2018). A photograph of samples of expanded Kulantau vermiculite is shown in Figure 1

Figure 1. Photo of expanded Kulantau vermiculite samples

According to standard methods, the qualitative characteristics of the vermiculite from the Kulantau deposit were determined, which are shown in Table 1.

Table 1 - Qualitative characteristics of vermiculite of the Kulantaus deposit

Sample No.	Humidity, %	Degree of hydration, %	Volume weight, kg/m3	Vermiculite content, %
1	6,2	65	178	30
2	9,0	70	200	35
3	3,7	60	130	28
4	3,1	75	140	26

The chemical composition of vermiculite is variable, % MgO - 14-15, FeO - 1-3, Fe2O3 - 3-17, Al_2O_3 - 10-17, SiO_2 - 34-42, H_2O - 8-15, there are also impurities such as Ti, Ni , Zn, Cu, Na, K.
Interlayer and interpacket gaps of the vermiculite structure can be considered as lamellar micropores with sizes of 0.3 - 1.2 nm /10.9/. The cation exchange capacity of vermiculite is in the range of 100-150 Meq/100g, that is, among clay minerals, it is one of the most exchangeable (Kaldybekova et al., 2018)
.

3. Results and discussion

Adsorption purification is based on the property of adsorbents to absorb undesirable impurities present in oils on their surface. In the process of adsorption and purification of vegetable oils, a significant amount of peroxide compounds, dyes, as well as some of the phospholipids and sodium soaps of fatty acids remaining in the fat after hydration and alkaline refining are removed.
The process includes mixing the oil with the adsorbent, holding for a certain time at a certain temperature under vacuum with stirring to ensure the adsorption process, and separating the adsorbent from unwanted components from the oil by filtration.
In the production of porous adsorbents, one of the main tasks is the creation of high porosity, which is also characterized by a uniform distribution of pores over the volume of the layer (Bezdenezhnykh et al., 2017).
Considering some aspects of mathematical modeling of the geometric structure of porous adsorbents, it is possible to regulate rheological properties when obtaining highly porous adsorbents, which are carried out by a complex of various techniques: external influences on structured mixtures, in particular vibrations causing a thixotropic effect, or the introduction of surfactants, temperature changes, etc.
The removal of the blowing agent is based on the evaporation or burning out of the blowing agent, which occurs during medium or high temperature exposure. (Kaldybekova et al., 2017). Water, volatile liquids, burnable solid additives are used as blowing agents. While using burnable additives, as a rule, a cellular porous structure is formed, while using evaporating liquids, a porous-capillary structure is formed.
If the mass concentration of the pore former in the material and the mass concentration of the structure-forming material are known, then the porosity of the resulting material can be calculated by the formula

$$\varepsilon = \frac{C_p / \rho_p}{C_p / \rho_p + C_m / \rho_m} \quad (1)$$

where

ρ_p and ρ_m - are the densities of the blowing agent and the structure-forming substance, respectively.

The loose packing method is used in the manufacture of fibrous and granular highly porous materials. Regarding fibrous materials, this method is based on felting, i.e., on the entanglement of fibers and retention of the shape given to the product due to friction and meshing of the fibers with each other. As a result, a fibrous porous structure is obtained, the characteristics of which depend on the thickness and length of the fibers used, and the preservation of the original properties depends on the elasticity of the fibers. An increase in the total porosity is predetermined, first of all, by using a monofractional composition of grains, and a decrease in the characteristic pore size by a decrease in their average size.

One of the most widely used methods is swelling. This method is based on the release of a gas phase in the plastic viscous mass or the introduction of a gas phase into it in the form of hydrogen, oxygen, carbon dioxide, water vapor, air, isopentane, freon, etc. As a result of saturation of the mass with a gas phase, its volume increases - swelling occurs (foaming).

A dispersed system is formed - air in the "liquid", hardening during further technological processing. During swelling, a cellular porous structure is formed, the total volume of porosity of which depends on the amount of the gaseous component introduced and retained by the mass. The decisive influence on the parameters of the porous structure is exerted by the rheological characteristics of the porous masses. Common to all varieties of swelling is the plastic-viscous state of the porous masses during their porousization, i.e., the porous masses must be able to irreversibly deform (flow) without discontinuity.

There is the only material which swelling occurs without its transition to a plastic-viscous (pyroplastic) state - vermiculite (Kaldybekova et al., 2018).

Vermiculite is a mica–like magnesia-ferruginous aluminosilicate of unstable chemical composition with an expanding structural cell belonging to the group of trioctahedral hydrosludes (Figure 3).

Figure 3 - Vermiculite deposits in nature.

Vermiculite is a secondary mineral formed as a result of exchange reactions, hydration processes, and other changes in magnesian ferruginous mica (biotite, phlogopite). In addition to chemically bound water, vermiculite micas contain a certain amount of zeolite water (in the form of a solid solution) and significant amounts of water adsorbed on the surface of the flakes.

In Kazakhstan, in Turkestan region, a number of vermiculite deposits have been identified and partially explored, of which the Kulantau, Iirsu, and Zhylandy deposits are the most promising (Kaldybekova et al., 2018)

An analysis of domestic and foreign literary sources showed that one of the effective areas of application of expanded vermiculite is its use as an adsorbent. However, theoretical studies of the process of expanded vermiculite, the flow of liquid through the structures of layers of expanded vermiculite have not been previously performed. The urgency of the problem increases in connection with the use of Kazakh vermiculites in the work, unexplored both scientifically and in practical terms.

As it is known, when vermiculite expands, lamellar porosity is formed due to the separation of mica plates by interpacket water, which turns into a vapor state when the vermiculite particles are heated to high temperatures. Therefore, the description of the structure of a porous material based on vermiculite requires the use of dynamic models, including the stages of vaporization in the interpacket space and the reorientation of mica elements under the pressure of the formed vapor.

The temporal evolution of the porosity of the material during the swelling of vermiculite can be described by a logistic function of the type:

$$\varepsilon = \varepsilon_0 + \frac{\varepsilon_1}{1+\exp(-t/\tau)}, \tag{2}$$

where

ε_0 - - initial porosity before the swelling process;

ε_1 - - "resource" of porosity, due to reorientation, expansion, and warpage of mica plates;

τ - characteristic time of intense swelling, determined by the intensity of the thermal regime.

For granular monofractive materials, one of three types of packaging is implemented: octahedral, tetrahedral and rhombohedral.

If, with octahedral packing, the number of grain layers per unit thickness of the material is equal *k*, then the specific porosity of the layer is determined by the formula:

$$\varepsilon = 1 - \frac{\pi k}{3\sqrt{2}\left(\sqrt{2}-1+k\right)}. \tag{3}$$

In using fibrous materials, the regular stacking model does not provide an adequate description of the structure of the porous layer. It is established that the porosity fluctuation in this case obeys the Gauss law with average porosity with good accuracy $\bar{\varepsilon}$:

$$W(\varepsilon) = \frac{1}{\sqrt{2\pi}\Delta}\exp\left[-\frac{(\varepsilon-\bar{\varepsilon})^2}{2\Delta^2}\right], \tag{4}$$

In the case of using a porous binder in the form of foam, the material is obtained with cellular porosity, consisting of the grains porosity and the binder porosity:

$$\varepsilon = \varepsilon_m + \varepsilon_s. \tag{5}$$

The results of the internal structure of adsorption layers studies using methods of adsorption isotherms allow us to conclude that the inner surface of a porous layer is characterized by an extremely complex developed shape and can be described by methods of fractal geometry (Kaldybekova et al., 2018)

At the same time, the inner surface of the layer is characterized by a fractal dimension *D* higher than the "usual" geometric dimension of the surface:

$$2 \le D \le 3. \tag{6}$$

The specific value of porosity and the inner surface depends on the initial geometric characteristics of the layer, i.e. the size of the granules and the way they are laid and the size of the molecules deposited in the layer.

The characteristic size during swelling is of the order of the average grain size ~*l* . At the length scale $\delta \sim l$ determined by the smallest adsorption area,

$$\sigma_{\min} \approx \delta^2 \tag{7}$$

the amount of substance adsorbed in a layer with a fractal surface will vary according to the law:

$$n \sim \delta^{-D} \approx \sigma_{\min}^{-D/2}. \tag{8}$$

The main issue thus comes down to determining two characteristics of the layer: the minimum adsorption σ surface, which is related to the porosity of the layer, and the fractal dimension D , which depends on the size and method of stacking the granules. The following estimates can be made.

Let be R - some characteristic radius of the sphere circumscribed around the grain. This size is determined in such a way as to take into account the size of the grain, the layer of the substance adsorbed on it, and the neighboring adsorbent grains in contact with this grain. Then the characteristic volume is defined as usual:

$$V \sim R^3. \tag{9}$$

And to estimate the characteristic free surface around the grain in the fractal layer S of the adsorbent, we can write the relation:

$$S \sim V^{D/3},$$ (10)

From here we obtain the relation for the specific surface:

$$s \sim R^{D-3}.$$ (11)

The radius R can be estimated from the following considerations (Kaldybekova et al., 2018).
Considering a grain approximately as an ellipsoid with three characteristic dimensions, we obtain for its volume:

$$V = \pi \frac{d_1 d_2 d_3}{6}.$$ (12)

It is necessary to take into account the correction for the volume of the adsorbed monomolecular layer of molecules:

$$\Delta V = l_1 F V^{2/3},$$ (13)

where F- is the grain shape factor.
Then R we find from the condition that the hypothetical sphere is equal to the volume , i.e. $V + \Delta V$

$$R \approx \sqrt[3]{V + \Delta V}.$$ (14)

The evaluation of the porosity of a layer of lamellar adsorbent, in particular, vermiculite, taking into account two characteristic scales, can be made based on the following relationship:

$$\varepsilon \approx (l_1/l_2)^{3-D}.$$ (15)

From this, one can obtain an estimate of the fractal dimension of the expanded vermiculite. Indeed, from the condition for the completion of the swelling process: $t \approx \tau$ we have:

$$\ln\left[\frac{\varepsilon_1}{(l_1/l_2)^{3-D} - \varepsilon_0} - 1\right] = -1.$$ (16)

As a result, we get:

$$D \approx 3 - \frac{\ln\left(\frac{\varepsilon_1}{1,4} + \varepsilon_0\right)}{\ln(l_1/l_2)}.$$ (17)

On the whole, the resulting porous layer is a cluster characterized by two parameters: the average radius $\bar{r}_N$ of developed adsorption and the width of the active zone ψ . For large numbers of particles that make up the layer N , the following relationship follows from the fractal theory:

$$\bar{r}_N \sim N^{\gamma} - N^{1/D},$$ (18)

γ - where a is an exponent that depends on the characteristic length.
The corresponding expression for the core width is also given by the fractal theory as the average distance between cluster branches:.
The corresponding expression for the core width is also given by the fractal theory as the average distance between cluster branches:

$$\psi \sim \bar{r}_N^{(3-D_F+\chi)/2},$$ (19)

where χ - is the index of the internal anisotropy of the adsorbent layer.
The thickness of the adsorbent layer can be used as the global characteristic length.
The fractal dimension of a cluster is determined by the physicochemical characteristics and conditions for the formation of a porous layer. Parameters: - the critical index and the degree of anisotropy may depend both on the physicochemical characteristics of the interacting substances and on the geometric characteristics of the

layer.The model presented in the work has sufficient generality and can be used both in organizing systematic experimental studies of porization and adsorption processes in highly porous adsorption layers, and in optimizing porization regimes.Industrial tests of expanded Kulantau vermiculite in the refining shop of LLP "Kainar-may" showed the possibility of its effective use for the adsorption and purification of vegetable oil instead of expensive imported bleaching clays.

4. Conclusion

As a result of experimental studies, it was found that vermiculite belongs to microporous sorbents with pore size changing during adsorption.It has been established that during the swelling of vermiculite, an increase in the adsorption capacity of vermiculite is observed, which leads to a sharp increase in their specific surface and the volume of transitional pores.

The results showed that the values of the acid number and the color of the purified oil decreased compared to the original oil. Moreover, the change in these indicators also depends on the temperature of thermal activation of the expanded vermiculite.

Acknowledgement

These studies were carried out with the support of the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (grant AP19679034 “Development of technology for producing bitumen materials for the road industry with the disposal of polymer waste in the technological process”)

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