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SORPTION PROPERTIES OF LATVIAN CLAYS AND ENVIRONMENTAL PROTECTION SURVEY

LATVIJAS MĀLU SORBCIJAS ĪPAŠĪBAS UN VIDES AIZSARDZĪBAS APSKATS

Vitālijs Lakevičs[1], Līga Bērziņa – Cimdiņa[1], Augusts Ruplis[2], Juris Pelšs[3]
1- Riga Technical University, RBIAC
3/3 Pulka street, Riga, LV 1045, Latvia
Phone :(+371) 67089275e-mail : lakevich@gmail.com, liga.berzina-cimdina@rtu.lv
2- Riga Technical University, Distance Education Study Centre
12 Azenes street, Riga, LV 1048, Latvia.
Phone: (+371) 2933 4332, e-mail: auruplis@latnet.lv
3- Latvian Institute of Organic Synthesis
21 Aizkraukles street, Riga, LV 1006, Latvia.
Phone: (+371) 2911-2851, e-mail: jura@osi.lv

Abstract. *The survey has been comprised in historical sequence. It has been attempted to group literature sources in a way that we consider to be the most relevant in the publication. Analysis of literature led to the following conclusions: during the last years most important and most advanced ways in investigations of Latvian clay surface characteristics have been found: Value determination of clay specific surface; Clay's porous structure investigation; Cation exchange capacity* determination; *Characteristics of organoclays; Catalytic characteristics of Latvian clays; Practical usage of clays in waste water treatment; Usage of clays in adulterants elimination from vegetable oils; Clays as catalysts in of organic compound reactions; New type of sorbent from rapeseed oil treatment waste. Experimental measurements supplement data base about surface characteristics of Latvian clay samples.*

Keywords: *adsorption, specific surface, porous structure, ion exchange, isotherm, clay.*

On the subject of accomplishment of material science at present particular attention is attracted by properties of such materials, which are in high dispersed position. Porous solids – sorbents and catalysts have intensively been investigated. Currently its role in decreasing of contamination of environment, weathering of construction materials and cultural monuments protection are realized.

Knowledge about properties of new high dispersed systems is deficient, because of emerging more new materials as well new opportunities for using well-known materials in unconventional industries.

Its investigation demarcates usage boundaries and navigates towards deepened penetration about connections between structure and specific operation properties.

Imposition of unconventional local natural clay minerals is theoretically motivated and live high dispersed system analysis from thermodynamic aspect.

In consecution of geological processes complicated chemical and physically chemical processes take place, in which results ensure widely distributed high dispersed aqueous rocks – clays.

They have high reserve of free surface energy which is potentially available.

It is unpretentious to do this by using clays as the sorbents: adsorption on clays occurs spontaneously. Until now this does not count much to keep a close watch.

Fonts of literature about sorption properties of Latvian clays are grouped in four parts: first articles; experimental measurements of the surface characteristics (specific surface area, pore

structure, determination of ion exchange capacity); field of usage (water pollution, air purification, rapeseed oil bleaching); dr. habil. theses, latest works.
The survey has been conducted in historical sequence. It has been attempted to group literature sources in a way that we consider being the most relevant in the publication.
The first articles about surface characteristics of Latvian clays have been shown in 1950s of the last century in works of professor J. Eiduks. First scientific work about sorption of organic stains as methylene blue, fuchsine and other on the samples of Latvian clays [1] has been published in 1951. Researches of pigment sorption were continued in a work of A.Vaivads and A.Upite, aimed onto determination of mineralogical contents of clay samples [2]. In 1973, professor J. Eiduks suggested research was published, and methanol gas sorption on Latvian clay samples has been measured for the first time [3]. It has been found that if the treatment temperature of samples increases, but value of specific surface area decreases.
More detailed results were analyzed in an article [4].
In the Soviet times, no great attention was paid to the sorption characteristics of Latvian clays. Only in 1991, research reports began to appear about Latvian clays surface characteristics. Systematic research has been made by A. Ruplis with collaborators. Docent of Latvian University, Rolands Bumans, also was involved in these works. Hexane and carbon tetrachloride **v**apor sorption isotherms were measured for aluminum oxide and aluminum hydroxide samples in order to determine their specific surface and pore structure parameters [5].
Specific surface of samples is one of the most significant parameters of disperse systems. There were numerous methods developed for detecting the specific surface; however nowadays the most widely used is the one based on analyzing gas or vapor physical adsorption [6, 7].
At first, experimentally measure adsorption isotherm of the analyzed sample. Using BET or Longmire equation, calculate amount of the adsorbed substance (sorbate) in a monomolecular layer a_m (mol/g). This internationally acknowledged BET method is used in various works for determination of specific surface of Latvian clay samples [3; 4; 8-10].
Sorption processes depend on pores of the samples. The most significant parameters of pores are total pore volume and pore volume distribution per radiuses or diameters [5]. These are determined by measuring adsorption-desorption isotherms. Various pore distribution calculation methods are based on Kelvin capillary condensation equation. Maximum of pore distribution curve demonstrates most frequently occurring pore radius (effective pore radius). Total pore volume is obtained by measuring adsorption of saturated vapor. In these conditions, adsorption isotherms of clay samples asymptotically approach ordinate axis, thus, total pore volume is detected by measuring amount of adsorption in pressure which is smaller than pressure of saturated vapors [11]. Usually, a pressure is chosen which lays within the relative equilibrium pressure interval between 0.90 and 0.98 [4; 12].
In numerous works [6;13-16], changing sorption parameters by thermal treatment or modified by mineral acids [17-20] is investigated. It was found that after a thermal treatment, specific surface and total pore volume of Latvian clays is descending [21; 22]. After modification with acids, specific surface and pore volume of samples is changing depending on acid concentration: increasing concentration, specific surface also increases, reaches its maximum and then descends. Changing of pore volume amount has the same nature [8; 23]. It was realized that acidic treatment of Latvian clay samples results in sorbents of energetically homogenous surface. These sorbents are used in gases and gases – liquids chromatography practices. In scientific work [24] attention is focused on sorption of humic substances on clays from Latvia deposits.
The results of works were summarized in A. Ruplis habil. doctor’s work in 1998 [25].

Determination of cation exchange capacity must be specially accentuated. This characteristic is significant in analyzing different unacceptable (toxic, radioactive) adulterant migration in over ground and ground-waters in normal or catastrophe created situations, it will open up the new opportunities for scientific motivated usage of sorbents for waste water treatment [26] and other.

Capacity amount of clay ion exchange plays a great role in various processes, however, for Latvia the most important are those related to soil fertility and environment pollution problems. Numerous methods were developed ion capacity determination of sorbents. In the middle of nineties, lots of attention was focused onto cation exchange capacity determination of Latvian clay samples by using organic pigments (methylene green, methyl violet).

Ion exchange capacity of Latvian clays is an important parameter of processes in which clays are used as sorbents at water solutions. It is determined and described in various scientific works [27-30].

In a bulletin [28], attention is focused onto method of measuring adsorption of methylene blue. It was found that amount of adsorption changes during shaking of clays and liquid (from 2 to 48 hours) depending of sample characteristics. At samples treated with mineral acids, adsorption of methylene green decreases in proportion with acid concentration.

It was found that, p – nitro aniline is not adsorbed on Latvian clays from water solutions. It adsorbs weakly on the samples, whose surface is partially covered with rapeseed oil coking products [27]. In scientific work [26], opportunities of using natural and thermally treated clay samples (from 200 to 800 ^{0}C) from Suntaži, Laža, Veldze and Kuprava deposits for cleaning wastewater are researched. The highest adsorption ability is characteristic for clays from Kuprava deposit, and it's explained by its mineralogical properties and small amount of additions. It's said that the active component in the clay composition is hydro muscovite. Chrystallic chemical structure of clays decomposes in – 500-600 ^{0}C temperature [26], and its destruction is accompanied by reducing adsorption ability. Clays from Veldze deposit, both natural and at 600 ^{0}C thermally treated, show good sorption abilities by cleaning wastewaters at "Reagents" and "Grindeks" companies. Meanwhile, clays from Kuprava are successfully used in cleaning technological wastewaters in Valmiera glass fiber production plant from non-ionogenous surface active substances, oil products, formaldehyde. [31] talks about cleaning of wastewaters containing phenol and formaldehydes using Latvian clays In the same time, it was discovered that Latvian clays may be used as catalysts in organic synthesis [32-34].

It was found that Latvian Quaternary (Priekules and Nicgales) and Devonian (Kupravas) clay samples can be used as effective catalysts in organic synthesis reactions, where final product is anticancer agent (1,4-butanediol dehydration reaction) [34].

Searching for new catalyst carriers is vital for improving of synthesis of several very important medicals [35] and further development of catalysis theory which is closely related to research of adsorption-desorption mechanism and issues of sorbent modifications [36].

Cation exchange in clay minerals depending of length of sulphuric acid treatment is researched in work [37]. It was stated that treating clay with 25% sulphuric acid for 1 hour is effective and improves its adsorption capabilities [37]. In article [38], it is informed about adsorption of lead ions from water solution at clay plates, but [39] – about lead ions adsorption from water solutions at scorched clay pellets. In article [40] are shown sorption properties of Kuprava clays – illits. [41] informs about using Latvian clays in air cleaning.

Academician E.Gudriniece with collaborators signified the idea about the rapeseed oil purification on Latvian clay samples [42; 43]. Discoloring, or bleaching is one of the refinement stages of vegetable oil. As a result, plant pigments like chlorophylls, carotinoids, etc are bound on sorbent's surface, also improving taste of the oil. Non-activated and thermally treated clay samples slightly improved number of rapeseed oil color, however, such oil does not correspond with nutrition oil standards. [44]. A. Ruplis and his scientific collaborators clarified, that samples of Latvian clays treated with mineral acids are useful for rapeseed oil bleaching [10; 44-46]. During process of bleaching, by-products appear. They are clays that contain 30-40% of rapeseed oil. By thermal treatment, a valuable product is obtained and it can be re-used in environmental protection [47; 48].

Obtained material finely adsorbs organic solvents from vapor phase, functioning as active coal. Materials produced from rapeseed oil bleaching by-products have good sorption parameters. This new type of sorbents are made of Latvian clay originated alum silicate matrix and rapeseed oil coking (250, 400 un 600 ^{0}C) products. Specific surface of studied samples is about 100 m^2 /g. They adsorb methanol and benzyl vapors at room temperature and demonstrate high thermal resistance [47]. Work [49] informs about obtaining silica gel-like sorbents from clays not containing carbonates.

At the end of 90-ies academician J. Freimanis developed his investigations about Latvian organoclays [50-52].

These are clays, whose metal ions are substituted by tetraalkilamonuim ions. They have higher interaction with oils and oily materials and they are capable to perform as powerful environmental cleaners, for example, against leakage of mineral oils [50; 53]. Also, these clays keep high turgescence ability and are widely used as thickeners for turning various oils into ointments, etc. [54]. Carbon tetrachloride and n-hexane vapor sorption increases in organoclays at the highest interval of equilibrium pressure. It can be considered that organoclays may colligate oleofilic molecules (petroleum, oils) from water/oils emulsions and water solutions [55]. Information about sorption of carbon tetrachloride vapors confirm the ability of organic cations to fix structure of plane parallel pores [56].

Analysis of literature led to the following conclusions: during the last years most important and most advanced ways in investigations of Latvian clay surface characteristics have been found:

1) Determination of value of clay specific surface.
2) Investigation of clay porous structure.
3) Determination of cation exchange capacity.
4) Characteristics of organoclays.
5) Catalytic characteristics of Latvian clays.
6) Practical usage of clays in waste water treatment.
7) Usage of clays in treatment of vegetable and other oils from adulterants.

Experimental measurements supplement data base about surface characteristics of Latvian clay samples. Experimental usage of clays: understanding adulterants distribution in natural conditions (soil, over ground and ground-water); waste water treatment, catalytic characteristics, treatment of vegetable and industrial oils, synthesis of new sorbents including organoclays).

Nevertheless, in comparison with clay samples investigation in other countries contribution of Latvian scientists is small and measurements about colloid chemical characteristics are at the beginning, in spite of indigenous clays significance in management of different processes of environmental protection, as well as in their usage in new and nontraditional branches.

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