MODIFIED CLAYS AND THEIR UTILIZATION FOR IMMOBILIZATION THE WASTE MATERIALS FROM WATER SOLUTION

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INTRODUCTION

The purification of waste waters contaminated by hazardous pollutants of inorganic and organic nature belongs among, serious problems of waste conservation, especially when such toxic materials as e.g., chlorinated phenols or polychlorinated biphenyls, contaminating the environment even in insignificant concentrations are involved. The elimination of such pollutants from water solution is an important problem not only from technical but economical point of view.

The development of sorbents of different type is solved by many institutions of research and commercial type. Active carbon, for example, is known as effective sorbent of toxic materials from water solution. It is sorbent regenerable by thermal desorption, however, there is a loss of important part of sorbent in each desorption cycle. This is the main reason of low economical advantage in its application. Therfore, the interest in development the sorbents of inorganic nature, utilizing the specific structure properties of some aluminosilicates among which also clay minerals belong, was significantly increased in recent years. It becomes apparent, e.g. that the sorbents based on clays belonging to smectite group are able to catch relatively effectively the inorganic and organic pollutants from water solution.

FEATURES OF CLAY MINERALS

Clay minerals are polycrystalline materials with very fine particles (0.5–5.0 μm) and layered structure. The structure is formed by tetrahedral and octahedral sheets being interconnected with oxygen atoms. Central cation of tetrahedra is Si^{4+} which may be substituted for Al^{3+}. Cations Al^{3+}, Mg^{2+} and Fe^{2+} are most frequent in octahedra. According to a number of interconnected sheets the clay minerals may be divided into two main groups. Into the first group belong those, forming the 1:1 layer as basic structural unit (one tetrahedral and one octahderal sheet). They are denoted as 1:1 phyllosilicates and their most konwn representative is kaolinite. Into second group belong clay minerals, which form the 2:1 layer (two tetrahedral sheets with opposite polarity, surrounding one octahedral sheet) as

basic structural unit. They are denoted as 2:1 phyllosilicates. Among them belong, e.g., micas, smectites and chlorites, differing in the content of interlayer space between individual 2:1 layers. For micas the non-hydrated cations (e.g. K^+, Na^+, Ca^{2+}) are fixed within the interlayer. The hydrated cations are placed between the 2:1 layer for smectites as the interlayer material. For chlorites, the interlayer materials form interlayer octahedral sheet where anions are represented by hydroxyl groups and Mg^{2+} anf Fe^{2+} are most frequent as central cations of octahedra.

The large surface of clay minerals (small dimensions of particles), layered character of their structure and in some cases also the presence of hydrated exchangeable cations within the interlayer (e.g. for smectites), enable not only the effective sorption of metals and organic substances on the surface of these porous crystals but also their fixation within the interlayer space.

Among technologically important clay minerals belongs montmorillonite (group of smectites), structure of which is illustrated on Fig. 1. In the following text, montmorillonite will be marked as MMT and its general crystallochemical formula can be written as

$$(Al_{4-y-z}Mg_zFe_y^{3+})^{VI}(Si_{8-x}Al_x)^{IV}O_{20}(OH)_4$$

$$(Me_{x-z}.nH_2O),$$
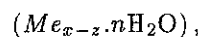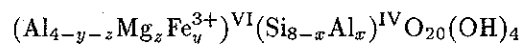
where x = number of central Al^{3+} atoms in tetrahedra, y = number of central Fe^{3+} atoms in octahedra, z = number of central Mg^{2+} atoms (or Fe^{2+}) in octahedra, Me = hydrated interlayer cations (K^+, Na^+, Ca^{2+}, Mg^{2+}).

The exchangeable interlayer cations have expressive hydration abilities and they are wrapped around by molecules of water being bound by hydrogen bonds on the surface oxygen atoms of the tetrahedral sheets of the 2:1 layers. The interlayer water, in dependence on moisture of environment and temperature influences then distance between the neighbouring 2:1 layers. This circumstance enables the expansion of structure which is the basis for majority of technological applications. The mentioned properties support also an effort to modify the MMT structure in order to enlarge not only the surface of amineral but also to get such material in the interlayer space of MMT which
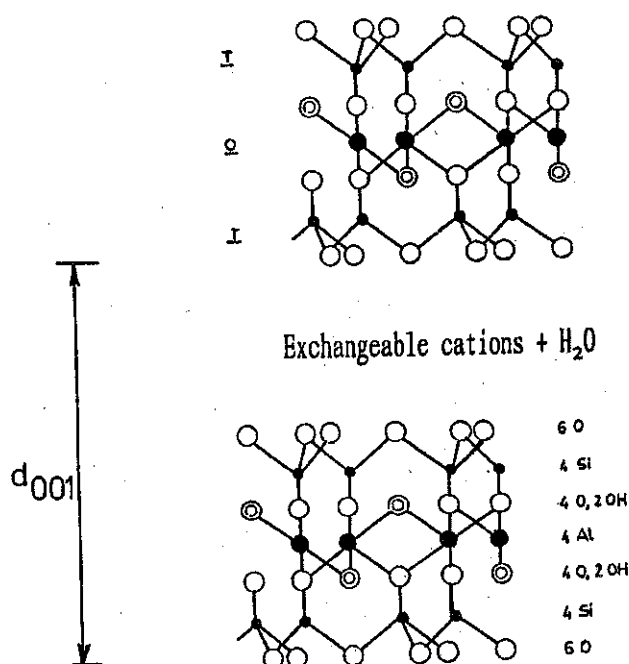
Exchangeable cations + H_2O

6 O
4 Si
4 O, 2OH
4 Al
4 O, 2OH
4 Si
6 O

Fig. 1. Schematic representation of montmorillonite structure. Tetrahedral and octahedral sheets are marked as T a O, respectively. Depending on amount of H_2O molecules and nature of the interlayer hydrated exchnageable cations the interlayer distance d_{001} ranges from about 12 Å to 15 Å.

will form a permanent porous crystal with defined dimensions of pores.

SORPTION OF METALS ON CLAY MINERALS

Heavy metals may be contained in waste waters or may be leached into water solution during the deposition of waste materials. In water reservoirs certain trace amount of metals is contained also as "geochemical natural background". In clay minerals, forming approximately 20% of upper lithosphere, natural accumulation of heavy metals may take place.

The sorption capacity of clay minerals for metals was studied by many authors. For instance, Borovec [1], [2] studied the sorption of heavy metals (Cd, Zn, Mn, Co, Ni, and Cu) on kaolinite, illite and montmorillonite, which were transformed to homoionic form by means of the intensive saturation. He found that the amount of metal sorbed from a solution depends on a type of clay mineral and pH of the environment. The sorbed amount is directly proportional to the size of total surface of clay and its exchange capacity and increases, with decreasing acidity of solution. Helios-Rybicka [3] found that the effectiveness of sorption of Zn, Cd an Mn in solutions with low concentration (1–140 ppm) is 80–98%, when using natural smectite as sorbent. Kaolinite showed lower efficiency. For smectite, the layer-charge appears to be as the main factor

affecting the sorption, whereas for kaolinite it is the existence of surface "active centers". Gracia-Miragaya et al. [4] showed that for effectiveness of sorption of heavy metals from the solutions (in concentrations which it is possible to expect in environment), first of all the type of sorbed cation is conclusive, both for kaolinite and the MMT. In spite of the fact, that the mechanism of sorption of metals on clay minerals is very complicated, we will try to make certain generalization and to express according to available sources (e.g. Farrah et al [5]) and own knowledge a measure of sorption capactiy of selected metals for three basic types of clay minerals by following sequences:

Kaolinite: Mg > Cu > Ca > Pb > Cd > Zn
Illite (clay white
mica):   Ca > Pb > Mg > Cd > Cu > Zn
Montmorillonite: Ca > Zn > Cu > Pb > Cd > Mg

In all cases, the amount of sorbed metal decreases with decreasing pH.

It may generally be said that for effectiveness of sorption of inorganic and organic compounds on clay minerals, the existence of "active centers" is important, both within the structure (hydrated interlayer exchange cations for smectites or vermiculites) and on the surface. The later originated on the surface of grains, e.g., in mechanical failure of the bonds between cations and oxygens of tetrahedra and octahedra. The activity of surfaces originated by crushing of mineral decreases with time owing to gradual saturation of loose bonds originated by mechanical failure. The activity of surface is not uniform in all of its parts.

The location of charges within the crystal structure of clay minerals, as well as the type and number of cations and anions, which may balance a charge deficiency within the crystal structure, play also important role for sorption properties. The cations from the solution are easily attracted by local electrostatic charge, balancing so the charge deficiency. In "active centers" the ion-exchange reactions are taking place and the exchange capacity of clay mineral is connected with a number of "active centers" of mineral. A measure of number of exchange centers and thus also of sizes of electrostatic charge of sturcture is the cation exchange capacity of given clay.

For kaolinite the 1:1 layers of which are connected between themselves by hydrogen bonds, the exchange cations are bonding in surface centers only so that for its a sorption properties the size of surface is important. The cation exchange capacity ranges from 0.03 to 0.18 mole.kg^{-1}. Besides the size of grains the exchange capacity is also influenced by the degree of structure disorder and it decreases with decreasing of the degree of structure disorder.

For smectites the 2:1 layers are deficient in positive charges and the cohesion of the 2:1 layers is given by interlayer hydrated cations. For example, for montmorillonite which belongs among dioctahedral smectites, the predominance of negative charges on the 2:1 layers is caused on an average from 70% by substitution of bivalent cations for Al in octahedra and from 30% by Al substitution for Si in tetrahedra. The total charge deficiency of the structure is balanced by exchange cations within the interlayer (structural centers) on an average from 80% and on the surface centers from 20%. The exchange capacity ranges from 0.60 to 1.50 mole.kg^{-1}.

SORPTION OF ORGANIC COMPOUNDS BY MODIFIED CLAY MINERALS

Organic molecules may be adsorbed on the surface of clays through various mechanisms (see e.g., Chiou et al. [6]). With regard to hydrophylic nature of clays however, they are relatively poor sorbents of non-polar organic molecules and for this reason the research works were directed towards the suitable modes of modification of clay minerals in order to utilize at best their large surface (e.g., Boyd et al. [7]). So, for instance, Chapman et al. [8] showed, that smectitic clays modified by intercalation of organic molecules into the interlayer may serve as relatively effective sorbents of chlorinated phenols, representing one of the groups of important and hazardous pollutants.

As it was told already, the effectiveness of sorption of clay minerals may be increased by modification of their structure. In presented work we will try to give a brief outline of two types of modification, i.e. intercalation of organic molecules and intercalation of large inorganic polycations into the interlayer of montmorillonite. Generally, the modification of clays is the subject of many interesting papers and represents a very extensive theme which cannot be discussed adequately here. For these reasons we will restrict ourselves to selected problems only.

ORGANICALLY MODIFIED CLAYS

Among well known organically modified clays belong n-alkylammonium clay complexes which were studied by Weiss and Lagaly [9]. These were prepared through intercalation of n-alkylammonium molecules into the interlayer space of smectites and vermiculites. Alkyl chains within the interlayer can be arranged in this way, that the alkyl chains are approximately parallel with the basal plane of layers or they can be inclined by a certain angle towards the basal plane of layers (see Fig. 2). The interlayer distance d_{001} is 13.5 A for the first type, while the d_{001} value is significantly increasing for the second one. The d_{001} value

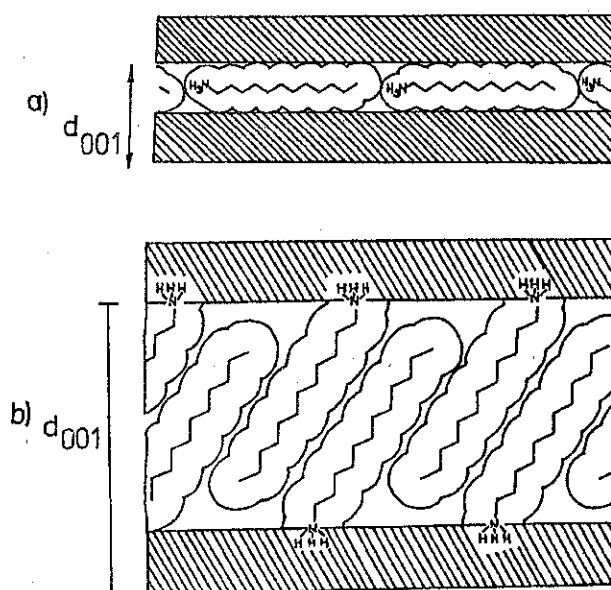*Fig. 2. Schematic illustration (after Lagaly and Weiss [21]) of two possibilities of location of n-alkylammonium molecules into the interlayer of 2:1 phyllosilicates: (a) alkyl chains are approximately parallel with the basal plane of layers and the interlayer distance d_{001} is 13.5 Å, (b) alkyl chains are inclined by a certain angle towards the basal plane of layers and the d_{001} value is significantly increasing in dependence on the magnitude of the inclination angle. The 2:1 layers are marked by hatching.*

can be directly measured by means of X-ray diffraction methods.

Other sample is modified MMT through intercalation by trimethylphenylamonium (TMPA) as organic cation; its preparation was described by Jaynes and Boyd [10]. In this way modified MMT is very interesting example, especially from the point of view of sorption of aromatic hydrocarbons from water solution. Before the intercalation by organic cation the natural MMT was saturated by Mg^{2+} ions and for some samples the Na^{+} and Li^{+} saturations in different ratios were used to reduce the charge. The success of modification depends also to some extent also on natural montmorillonite material which is selected for preparation. If we select, for instance, MMT Wyoming – a fraction below 2μm – it is possible to obtain the porous crystal with a size of specific surface over 200 m^2.g^{-1}. For MMT separated from bentonite of Jelšový potok locality this value was lower by 13%. In case of the clay-organic complex TMPA-MMT, and clay-inorganic-organic complex Li-TMPA-MMT the immobilization of aromatic hydrocarbons from water solution is directly proportional to the size of surface and indirectly proportional to the layer-charge (may be thanks to the adsorption on the surface of clays and amount of adsorbed substance). The inter-

calated TMPA molecules within interlayer are bonded to basal tetrahedral oxygens and the distance between the 2:1 layers is significantly increasing. After TMPA intercalation the d_{001} value for MMT without inter-layer water molecules is increasing from 10.4 Å to about 15 Å. Limit values of adsorption of selected aromatic hydrocarbons for the above mentioned types of modified MMT (TMPA-MMT and Li-TMPA-MMT) are shown on Fig. 3, where they are plotted against the plane size of molecules of aromatic hydrocarbons. The molecules were calculated from sizes of bond lengths, ionic radii and geometry of molecules.

modified), and in the second one, this clay is stabilized (after adsorption) through binding agent, which may be, e.g. cement or fly ash with lime.

In order to illustrate the effectiveness of stabilization of non-modified and organically modified clays we will submit the results obtained during the tests with oil muds (Evans et al. [11]). The samples of these muds had high content of organic compounds (average value of loss of ignition was approx. 90%) and pH value ranged from 1 to 5. For testing was used ratio between oil muds : clay : binding agent = 1 : 0.4 : 0.4. Commercially manufactured non-modified and organically modified clays were tested and as stabilizer a mixture of 3:1 fly ash and lime was used. After immobilization process the content of oil materials in aqueous leachants, abtained from stabilized clays by means of TCLP method (Toxicity Characteristic Leaching Procedure, EPA SW-846 Method 1310), was analyzed by gas chromatography. Average values of concentration of total organic compounds (including scattering within the scope of 95% reliability interval) for stabilized organically modified and non-modified clays are illustrated on Fig. 4. From obtained results it follows, that in comparison with non-modified clays the organically modified clays (both stabilized) bind organic compounds from oil muds about three times better.

Besides the determination of total organic compounds, relatively important criterion is the phenol content in TCLP extract. Phenol is often represented in these muds and usually also in the other organic wastes, and moreover is relatively mobile component, so that the determination of its content in extract
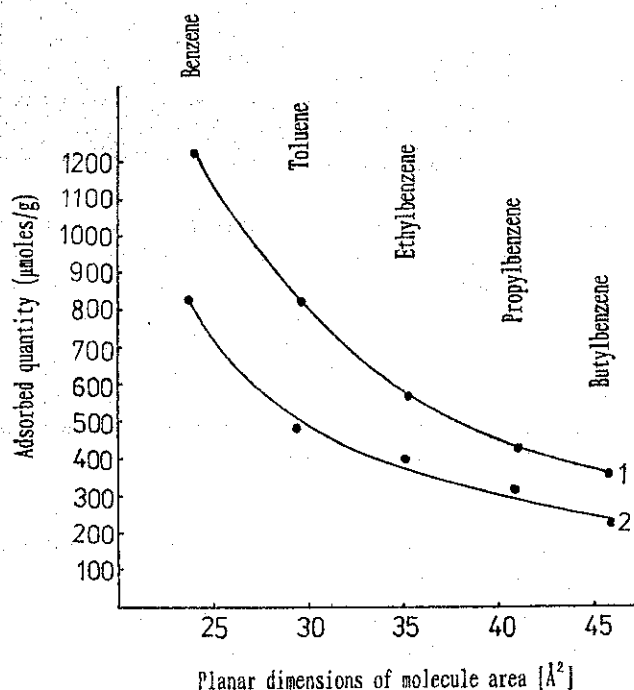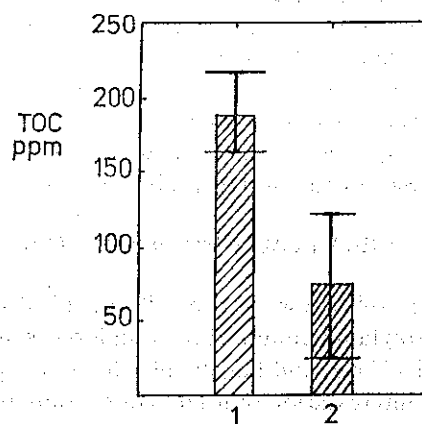

Fig. 3. Dependence between the limit values of adsorption of selected aromatic hydrocarbons and the plane size of molecules for modified montmorillonites: (1) Li-TMPA-MMT with the size of specific surface 239 $m^2.g^{-1}$, (2) TMPA-MMT with the size of specific surface 109 $m^2.g^{-1}$. Graphical representation was composed using data of Jaynes and Boyd [10].

Besides above mentioned examples also many further applications exist and for adsorption of pollutants from water solution it is possible to utilize clays (both modified and the non-modified), which are produced commercially. The market offers at this time a great number of these materials. There are for instance, non-modified clays as bentonite, montmorillonite, but also organically modified clays on the basis of quarternary ammonium ions, bearing the commercial names as bondtone, claytone, suspendtone, etc.

A proper immobilization of hazardous pollutants has two phases. In the first one, the respective pollutant is adsorbed on clay (non-modified or organically

Fig. 4. Average values of concentration of total organic carbon (TOC) in the TCLP extracts from non-modified (1) and organically modified suspentites (2) stabilized after adsorption of organic compounds from oil muds by mixture of fly ash and lime. Average values and standard deviatione were calculated according to data of Evans et al. [11] for three samples of different type sorbents.
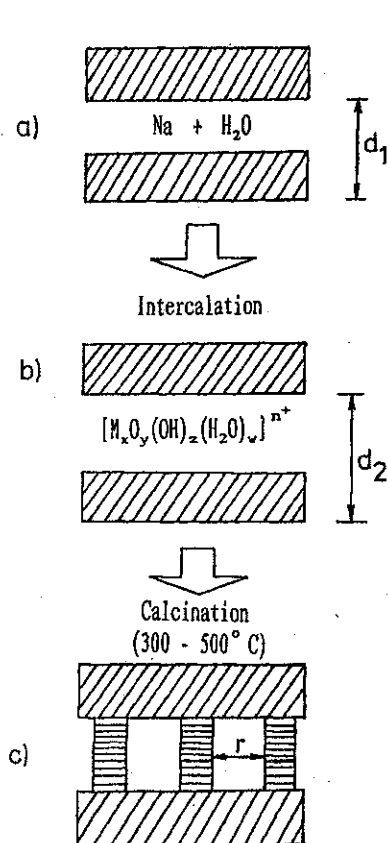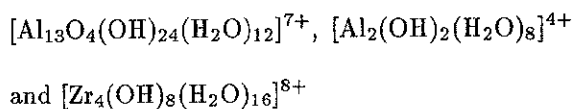
Fig. 5. Scheme for preparation of pillared montmorillonite as thermally stable porous material. (a) Na-form of MMT (2:1 layers are marked by hatching). The d_1 value represents the interlayer distance before intercalation (12–15 Å). (b) Intercalation by inorganic polycation where the d_2 value represents the interlayer distance after intercalation (16–22 Å). (c) Calcination and formation of interlayer "pillars" (hatching of those is parallel with the plane of 2:1 layers); their distance is marked by r.

$$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}, \quad [Al_2(OH)_2(H_2O)_8]^{4+}$$

and $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$

After transforming the original clay (MMT) to Na-form (by saturation of Na^+ ions) the intercalation by polycations is performed. The subsequent calcination at about 300–500° C will form thermally stable porous structure, which is given by origin of interlayer pillars perpendicularly to the plane of layers (Fig. 5). Unlike zeolites, the pillared MMT bears two-dimensional pore system which indicates its layered structure. Pores originate only in the direction parallel to layers; they may not originate in the direction perpendicular to layers. It may generally be stated, that effective diameter of pores for zeolites ranges from 2.0 Å to 7.6 Å and for pillated MMT is higher, ranging approximately from 7.0 Å to 12 Å. The size of pores is possible to modify according to the size of intercalated cation into the interlayer. Modification by
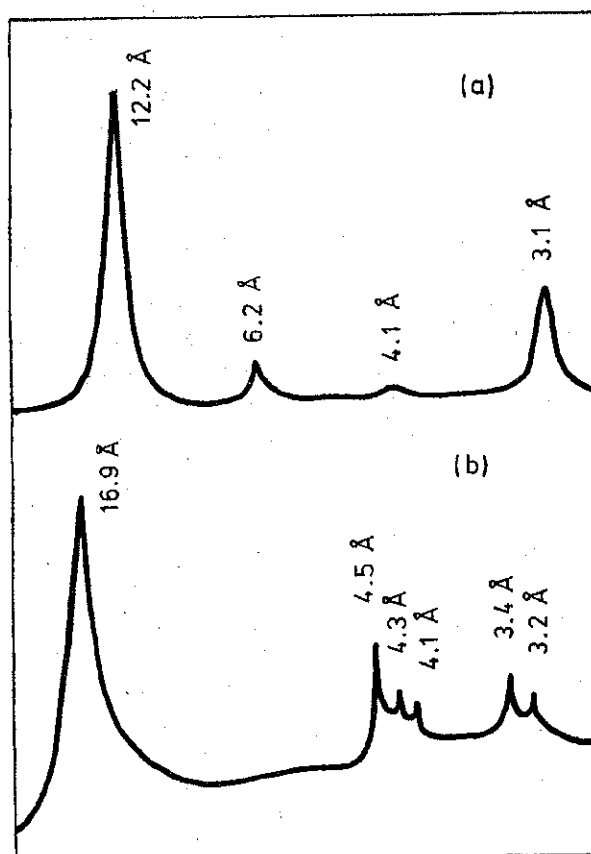
may serve as indicator of effectiveness of stability for organic wastes. The tests showed that the conclusions given for total organic compounds are roughly valid also for phenols.

PILLARED CLAYS

As the second mode of modification of clays appears the intercalation of those by large inorganic cations into the interlayer space (see e.g. Brindley and Tsunashima [12], Pinnavaia [13]). Among the important properties of pillared calys belong that they are thermally more stable (approx. up to temperature 500° C) than the organically modified ones. In works published up to the present (e.g. Sterte [14], Figueras et al. [15], Krajovič and Horvát [16]) greatest attention is given to preparation and properties of pillared smectites intercalated by the following polycations:

Fig. 6. Comparison of X-ray powder diffraction patterns natural montmorillonite (a) and Al_{13}-pillared montmorillonite (b). Experimental conditions: oriented samples, diffractometer INEL with the curved position sensitive detector, reflection mode, $Cuk\alpha_1$ radiation, Ge monochromator).
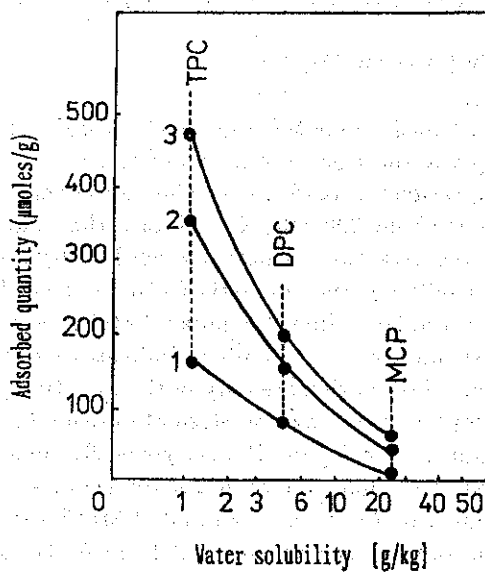
Fig. 7. Adsorbed quantity of 3,4,5-trichlorophenol (TCP), 3, 5-dichlorophenol (DCP) and 3-monochlorophenol (MCP) by surfactant-modified Al_{13}-pillared montmorillonite plotted against their water solubility for three different equilibrium concentrations of chlorinated phenols in solution: (1) = 200 μmoles.l^{-1}, (2) = 450 μmoles.l^{-1}, (3) = 700 μmoles.l^{-1}, at pH=6,5 and 255 mg of surfactant (Tergitol 15S-5) per gram of clay. The graph was composed according to data of Michot and Pinnavaia [20].

pillaring enlarges significantly the size of clay surface approximately up to 500 m^2g^{-1}.

After intercalation by large polycations (and subsequent calcination) the d_{001} value for pillared MMT is increasing from approximately 12 Å (for natural MMT) about 17 Å (for Al_{13}-pillared MMT). The d-values can be directly measured using X-ray diffraction method and, therefore, this method can be used for evaluation of intercalation process. To visualize differences between natural nad pillared MMT their X-ray powder diffraction patterns are compared on Fig. 6.

Many works dealt with given processes or modification in order ot utilize the pillared clays as catalysts (e.g., in cracking processes, where large molecules of 1-isoprophyl-naphthalene type cannot diffuse, for spheric reasons, into porous system of zeolites). The trend of application of pillared clays is very perspective at present, which confirms also the fact that in 1988 the independent number of Catalysis Today journal was dedicated to this problematics.

The utilization of pillared MMT in sorption the ecologically toxic substances from their aqueous solutions seems also to be very promising. For instance, Zielke and Pinnavaia [17], or Srinivasan and Fogler [18], [19] studied the apllication of Al-pillared MMT to immobilize the chlorinated phenols. They found

that their large surface is, no doubt, very suitable for adsorption, on the one hand but their adsorption capacity is limited by their hydrophobic nature, on the other hand. This adsorption capacity is, indeed, higher than that of non-modified MMT, which is practically negligible, but lower than the capacity of organically modified clay (Boyd et al. [7]].

Therefore, Michot and Pinnavaia [20] proposed a manner, how to increase the adsorption effectiveness of chlorinated phenols by Al_{13}-pillared MMT. They treated the surface of pillared MMT with surfactant, marked as Tergitol 15S-5 (alkyl polyethylene oxide) reaching, in this way, the increase of adsorption efficiency. The effectiveness was tested on four compounds, i.e., pentachlorophenol (PCP), 3, 4, 5-trichlorophenol (TCP), 3, 5-dichlorophenol (DCP) and 3-monochlorophenol (MCP). The solubility of these compounds in water, as well their polarity is decreasing with increasing number of substituted Cl. The adsorbed amount of mentioned
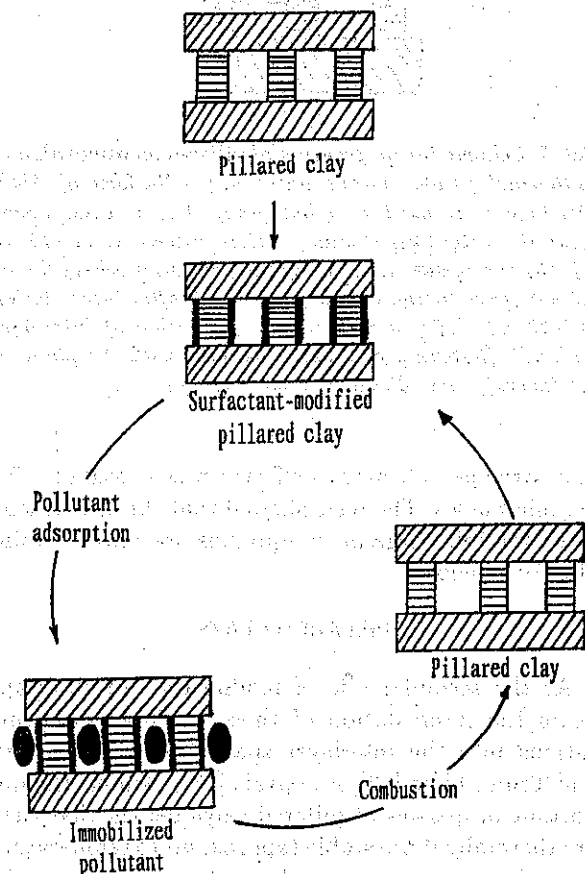

Fig. 8. Scheme for the thermal recycling of a surfactant-modified pillared clay (after Michot and Pinnavaia [20]), being used as adsorbent of organic pollutants. The surfactant is shown to occupy only microporous sites on the pillar surfaces.

phenols from water solution by surface-modified Al_{13}-pillared MMT (at given equilibrium concentration of phenols) was then increasing in the order: MCP<DCP<TCP<PCP. Fig. 7 illustrates the adsorbed amount for three types of phenols in dependence on their solubility in water (at given equilibrium concentration, at given pH and at given amount of surfactant by which the surface of pillared MMT was modified). Michot and Pinnavaia [20] found that the adsorbed amount of phenols is dependent on the volume of used surfactant per unit of clay, on pH of environment and, of course, also on phenol concetration in water solution. It is rather simplified to state that increased amount of surfactant influences positively adsorption of phenols from water solution. On the contrary, increasing of pH influences the adsorption process negatively.

The possibility of recycling the pillared clays after the immobilization processs of pollutants from water solution may be considered as very important for practical utilization. Michot and Pinnavaia [20] demonstrated that Al_{13}-pillared MMT with the surface modified by surfactant can be after adsorption of phenols thermally desorbed. Pollutants as well as the surfactant are thermally degraded and then again the original Al_{13}-pillared MMT is available for new cycle of adsorption process when the repeated treatment of its surface with surfactant is performed. The schematic illustration of mentioned cycle is given on Fig. 8.

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