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New Composite Materials in the Technology for Drinking Water Purification from Ionic and Colloidal Pollutants

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1. Introduction

Composite materials (composites) are inherently heterogeneous and represent a defined combination of chemically and structurally different constituent materials, ensuring the required properties such as mechanical strength, stiffness, low density, or other specific characteristics depending on their purpose. Therefore, composite material is a system composed of two or more physically distinct phases whose combination produces a synergistic effect and aggregate properties that are different from those of its constituents. Favorable characteristics of composite materials were known to the people even in the period BC (before Christ-Century) and were used in order to improve the quality of human daily life. For example, it is known that in the ancient period, people made bricks that were reinforced with straw, and thus secured greater longevity and durability of their buildings. The incorporation of the straw improves the strength, toughness and thermal insulation properties of these composites. In principle, the degree of reinforcement (volume fraction of straw) and the level of alignment of the straw stalks (and their lengths) may be adjusted so that not only the properties but their anisotropy may be optimised differently in various parts of the structure [1]. Significant development and application of composites began in the second half of the 20th century, wherein their diversity and areas of application are constantly increasing. Development of composite materials is resulted mainly from the increasing need for materials with better mechanical characteristics that would be used as components in various constructions. For this purpose, such composites should have an adequate strength, stiffness, good oxidation resistance and low weight. Intensive study of composite materials and their processing methods has caused that these materials replace metals and alloys and become indispensable in the manufacture of parts for automobiles, spacecrafts, sports equipment etc. In terms of exploiting modern engineering composites

this remains a central principle. Modern composites can be said to have "designed micro- and nanostructures" which means that the constituents of composites have much more finely divided structures and tend to have sizes in the micrometre or nanometre range. Basic factors affecting properties of composites are as follows:

- Properties of phases;
- Amount of phases;
- Bonding and the interface between the phases;
- Size, distribution and shape (particles, flakes, fibers, laminates) of the dispersed phase - reinforcement;
- Orientation of the dispersed phase - reinforcement (random or preferred).

Good bonding (adhesion) between matrix and dispersed phase provides a high level of mechanical properties of the composite via the interface. In addition, interfaces are responsible for numerous processes of electron transfers and play crucial role in redox processes, heterogeneous catalysis, adsorption etc. Usually, there are three forms of interface between the two phases within the composite:

1. Direct bonding with no intermediate layer. In this case adhesion ("wetting") is provided by either covalent bonding or van der Waals force;
2. Intermediate layer in form of solid solution of the matrix and dispersed phases constituents;
3. Intermediate layer (interphase) in form of a third bonding phase (adhesive).

Current challenges in the field of composite materials are associated with the extension of their application area from structural composites to functional and multifunctional composites. In this respect, a great improvement of composite materials through processing has been made enabling the development of composite materials for electrical, thermal and other functional applications that are relevant to current technological needs. Examples of functions are joining, repair, sensing, actuation, deicing (as needed for aircraft and bridges), energy conversion (as needed to generate clean energy), electrochemical electrodes, electrical connection, thermal contact improvement and heat dissipation (*i.e.*, cooling, as needed for microelectronics and aircrafts) [2]. Modern processing includes the use of additives (which may be introduced as liquids or solids), the combined use of fillers at the micrometer and nanometer scales, the formation of hybrids, the modification of the interfaces in a composite and control over the microstructure. Therefore, it can be said that the development of composite materials for current technological needs must be application driven and process oriented. The conventional composites engineering approach, which is focused on mechanics and purely structural applications, is in contrast to mentioned modern practice.

On the contemporary level of science development it is known that materials of certain characteristics can be obtained only by strictly defined procedures of processing and depend on their chemical composition and structure. Since composites are heterogeneous systems, as already has been noted, the matrix is of great importance whose structure and chemical

composition determine the most dominant features of the composite as a unit. However, it should be noted here that the composite does not possess properties of a single component but exhibits qualitatively new features, because of which it is considered as a new material. In addition to the dominant use of composites as structural elements, important application of composite materials is in the water purification technologies. In this field of application, composites usually have the role of adsorbent, electrochemically active materials, catalysts, photocatalysts etc. Bearing in mind that the material efficiency in the removal of harmful substances from water is higher if greater is its surface area, there are tends of scientists to develop these materials with required and defined nanostructures. In addition to the specific surface area increasing, nanostructured materials exhibit a qualitatively new properties compared to the related structure at the micro or macro scale. In this manner, it is developed specific procedure for certain metal hydroxides and natural organic matter layering onto alumosilicate matrix as well as procedures of microalloying which both lead to significant changes of the surface acido-basic and electrical properties of the alumosilicate matrix. The nano-scale composites provide an opportunity to study the phase boundaries and phenomena occurring at the surface, interface boundaries and within intergranular area during composites synthesis or during their interaction with aqueous solutions.

2. An overview and trends in use of composites in industrial plants

Nanocomposites based on polymers represent an area of significant scientific interest and developing industrial practice. Despite the proven benefits of polymer based nano-composites in the scope of their mechanical properties, and some distinctive combination/synergism of improved structural features, the real application remains still relatively isolated and not well discussed.

An insight in the historical (re)view on polymer nano-composites showed on the first type used based on the combination of natural fillers and polymers in the 90s [3-6] up to estimated 145 million USD spent at huge market of polymer based nano-composites in 2013 [7].

3. The concepts of interphase boundaries modification, microalloying and coating/layering in the composite synthesis

Methods and techniques for managing properties of composite materials include the selection and modification of constituent materials as well as changing the interface boundaries within the composite. Some composites are most commonly fabricated by impregnation (infiltration) of the matrix or matrix precursor in the liquid state into the appropriate filler preform. The connection between the constituents depends on the microstructure and chemistry of the interface boundary. The matrix and filler are connected by chemical bonds, interdiffusion, van der Waals forces and mechanical interlocking [2]. The first three interactions require very close filler-matrix contact that can be achieved if the matrix or matrix precursor wetting the surface of filler during the infiltration of matrix or matrix precursors in the filler preform. Effective wetting means that the liquid is evenly

distributed over the surface of filler, while a poor wetting means that the liquid drops formed on the surface. Wettability can be increased by applying the coatings, adding wetting agents or by chemical surface functionalization (the introduction of functional groups on the surface that increase wettability) thereby changing the surface energy. If the filler is carbon fiber, surface treatments involve oxidation treatments and the use of coupling agents, wetting agents, and/or coatings. Often, metals or ceramics are used as coatings for carbon fillers. Metallic coatings are usually formed by coating carbon fiber reinforcements with metals *i.e.* Ni, Cu and Ag. Examples of ceramic coatings are TiC, SiC, B_4C, TiB_2, TiN which are distributed by using Chemical Vapor Deposition (CVD) technique or by solution coating methods starting from organometalic compounds. Therefore, these are examples of application of coatings on carbon materials to illustrate the method of modification of surface properties.

In the case of metal-ceramic composites, certain liquid metals react with ceramic preform during infiltration. For instances, composites based on the Al–Al_2O_3 system can be obtained by Reactive Metal Penetration (RMP) method which is based on infiltration of ceramic preforms by a liquid metal, generally aluminium or aluminium alloys [8,9]. During the process, a liquid metal simultaneously reacts and penetrates the ceramic preform, usually silica or a silicate, resulting in a metal-ceramic composite characterized by two phases that are interpenetrated. Another example is the reaction between SiC and Al during the infiltration of molten aluminum in a preheated preform:

$$4Al + 3SiC \rightarrow Al_4C_3 + 3Si \qquad (1)$$
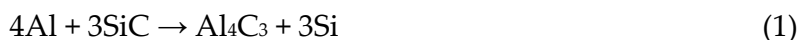
From the equation it can be seen that Si is generated during the reaction which is then dissolved in molten aluminum, while Al_4C_3 occurs at the SiC-Al interfacial boundary. The degree of reaction increases with increasing temperature. On the contrary, there are metals that in liquid state difficult wet the surface of the ceramic resulting in metal infiltration hindering. The difficulty of wetting and bonding of liquid metals to ceramic surfaces is related to atomic bonding in the ceramic lattice and can be improved by application of coatings. Coated particles (composite particles) are composed of solid phase covered with thinner or thicker layer of another material [10.11]. These coatings - layers on the surface are important for several reasons. In such way, the surface characteristics of the initial solid phase are modified and sintering conditions as well as molten metal infiltration can be better controlled.

As can be seen from examples, the processing of composite materials often involves high temperature and pressure to cause the joining of constituent materials forming a cohesive material. Generally, the matrix dictates the required temperature, pressure and processing time during composite synthesis. Sintering is an important factor in achieving the desired microstructure of ceramic based composites and includes very complex processes. In addition to surface coatings, an important influence on sintering has been exhibited by an addition of microalloying components, which significantly determine a microstructure and properties of ceramics [12]. The presence of small amounts of impurities in the starting material can vastly influence their mechanical, optical, electrical, color, diffusivity, electrical

conductivity, and dielectric properties of matrix. Microalloying, as a known modern procedure for changing the intrinsic semiconductor properties, by authors' original works (Purenovic et al.), get more and more important role in the control of some structurally sensitive properties of metals, alloys, ceramics, composites and other materials. It is known that the nature of matter is determined by its composition and structure. There are many structurally sensitive properties of materials, but among the most sensitive are the conductivity, electrode potential, magnetic, catalytic and mechanical properties. Microalloying means adding certain elements in small (ppm) quantities, thereby modified structure results in a significant change in the value of conductivity and the electrode potential. Conducted own investigation and the results obtained showed an excellent rational electrochemical behavior of composites such as microalloyed aluminum, microalloyed magnesium, as well as composite ceramics and quartz sand microalloyed with aluminum and magnesium, in contact with aqueous solutions of electrolytes or water which contain harmful ingredients in ionic, molecular and colloidal state. Microalloyed and structurally modified composite ceramics have high porosity (30%), with the macro-, meso-, micro- and submicropores. There is direct relationship between porosity and structure of these composite materials, especially when it comes to nanostructured fragmented crystals. It is worth to emphasize the domination of amorphous phases with crystalline substructure, which is impossible to be removed, and it would be inappropriate to be removed, because the contact of crystals with amorphous layer is responsible for numerous processes of electrons exchange. By certain processes and reactions in the solid phase, the amorphous microalloyed aluminum, microalloyed amorphous magnesium, amorphous-crystalline structure of composite microalloyed ceramics and amorphous-crystalline structure of microalloyed quartz sand could be obtained. Many metals, alloys and composite electrode materials manifested significant differences in the reversible thermodynamic potential and the steady corrosion potential.

The manufacturing processes used to make composite ceramics can cause the development of liquid phases during sintering, and their retention as remnant glass at triple junctions and along grain boundaries and interphase boundaries after cooling to room temperature. Formed thin intergranular films are relevant to creep behavior at high temperatures, and also responsible for the strength of the bonding at interfaces. However, the heat treatment at elevated temperatures which is used for joining constituent materials and establishing the cohesive forces shows a disadvantage because cooling can lead to disturbance of established bonds between phases. Namely, during the cooling, differences in coefficients of thermal expansion could result in unequal contraction by which established bonds are broken. This problem is particularly evident in metal-ceramic composites, where high temperatures are usually applied during synthesis.

4. Preparation of modern nano-composites

Processing of nanocomposites based on layered silicates is rather challenging activity to achieve the full technical and engineering potential, which is the field with the largest growth forecast [13-16]. The modification of silicates by use of organic components is

needed to allow intercalation, and also in order to improve compatibility/nano-distribution some additional ingredients have to be applied. The thermal treatment as step in processing sequence helps proper stabilisation of nanocomposites that has to take into consideration the oxidative stability of the polymer substrate, the influence of the nano-filler and the impact of modifiers and compatibilisers.

Montmorillonite of natural origin is among the most used nano-fillers. Traditional nano-fillers contain metal ions and other contaminants that may influence the thermooxidative stability and features of the nanocomposites. Organic modification of the (natural/traditional) clay is usually realized by cation exchange with a long-chain amines or quaternary ammonium salts. Content of such involved organic material content within the clay may be up to 40 mas.%. Therefore, the total thermal resistance of the composite material highly depends on the thermal stability of the organic ingredient. The thermal stability of the ammonium salts is limited at the processing temperatures applied (ex. extrusion, injection molding, etc.). Namely, thermal degradation of ammonium salts starts at 180°C and may be even tentatively reduced by catalytically active sites on the alumosilicate layer [17].

The compatibiliser applied as organically modified filler is often polypropylene-g-maleic anhydride in amount from 5 to 25% in the final composite formulation. The inferior stability of such low molecular weight filler comparing to the parent polymer affects the total stability of the final polymer based nanocomposites.

5. An improvement of composites stability

Nanocomposites may show higher stability due to increased barrier to oxygen, or lower stability because of undergone to hydrolysis through entrapped water [18,19]. In conventional practice stabilizer systems based on phenolic antioxidants and phosphites are applied, and in recent investigations new found components of filler degradation deactivators has been tested [20].

A traditional state-of-art polypropylene (PP) nanocomposite consisting of maleated PP and nano-clay is traditionally stabilized by a proven combination of phenolic antioxidant and phosphites. The polymer degradation may be completely prevented even after 5 extrusion cycles by using the patented stabilizer system AO-2 (based on oxazoline, oxazolone, oxirane, oxazine and isocyanate groups) [20], additionally improving mechanical properties of the resulting nano-composites and discoloration during processing and application.

The underlined thermal instability of the usual ammonium organic modifiers can be diminished by using the phosphonium, imidazolium, pyridinium, tropylium ions [21]. An alternative way to produce thermally stable nano-composites is the use of unmodified clays in combination with selected copolymers playing role of dispersants, intercalants, exfoliants and compatibilisers for PP nano-composites. In current processing of nano-composites different structures are identified such as polyethyleneoxide based nonionic surfactants [22] and amphiphilic copolymers based on long-chain acrylates [23]. Recently, more specifically poly(octadecylacrylate-co-maleic anhydride) and poly(octadecylacrylate-co-N-

vinylpyrrolidone) in the form of gradient copolymers are applied with unmodified montmorillonite for processing PP nano-composites. Such obtained nano-composites show partial exfoliation, the final visual appearance is similar to the classical ammonium modified systems, however better thermal and thermo-oxidative stability is proven [23]. The most important improvement is achieved in the mechanical vales comparing to the conventional polymer system.

6. Nanocomposites use in a competitive environment of the materials

Nanocomposites materials are very attractive from the scientific and practical point of view, although some other materials are also interesting, such as plastics, fillers, blends, and different additives fulfilling the specified product profile. In such competence, the lowest cost solution comprising acceptable material structure and properties/resistances would dominate. Even more, competitive (nano)composite materials would benefit from nanocomposites developments and keep their application fields with improved features. Most of nanocomposites materials applications are intended for long-term and outdoor use. This is important aspect on the need for relevant nanocomposites stability. Namely, it is known that inorganic fillers often show a negative effect on the oxidative stability to a varying extent. The interactions of the filler and the stabilizers over adsorption/desorption mechanisms are mainly responsible for the impact. The specific surface area of the filler and pore volumes, surface functionality, hydrophilicity, thermal and photo-sensation properties of the filler and transition metal content (ex. manganese, titanium, iron) have been found to be potential factors/elements of the interaction [24].

Polypropylene/montmorillonite nanocomposites, additionally stabilized with antioxidant, degrade much faster under photo-oxidative conditions than pure polypropylene [25,26].This phenomenon is attributed to active species/sites in the clay generated by photolysis or photo-oxidation, and by consequence interaction between antioxidant, montmorillonite and maleic anhydride modified polypropylene. In natural clay present iron may additionally play an active role in the dramatic modification of material oxidation conditions [27], and nanoparticles also catalyze the decomposition process [28]. The use of so-called filler deactivators or coupling agents is potential solution for diminishing the negative influence of fillers on the (photo)oxidative stability by blocking active sites on the filler surface. Amphiphilic modifiers with reactive chemical groups in the form of polymers, olygomers or low molecular weight molecules such as bisstearylamide or dodecenylsuccinic anhydride have been proposed [29].Thus, stabilizer systems containing filler deactivators should have an affirmative effect in nano-composites for long-term stability.

7. Nano-composites materials for water treatments: State-of-the-art and perspectives

Clean drinking water is essential to human health, and also so-called technical water is a critical feedstock in a variety of key industries including electronics, pharmaceuticals and

food processing industries. Taking into consideration that available supplies of fresh water are limited (due to population growth, extended deficiency, stringent health regulations, and competing demands from a variety of users/consumers) the world is facing with challenges to satisfy demands on high water quality standards and quantities (volumes). Benefits and trends in nano-scale science, chemistry and engineering impose that many of the current problems regarding green chemistry may be resolved using nano-sorbents, nano-catalysts, nanoparticles and nanostructured catalytic membranes. Nano-materials are characterized by a number of key physicochemical properties being particularly attractive for water purification treatments. Nanomaterials have much large specific surface area than bulk respect particles (mass to volume ratio), also they can be functionalized with reactive chemical groups specific in affinity to a given model compound. These materials may possess redox features and take part in shape- and structural-dependent catalyzed reactions of water purification. In aqueous solutions, they can serve as sorbents/catalysts for toxic metal ions, radionuclides, organic and inorganic solutes/anions [30]. Moreover, nano-materials can be used in selective targeting of biochemically constituents of aquatic bacteria and viruses. The nano-materials seems to be key components in future environmental friendly and cost-effective functional materials to desalinate public and polluted waters world-wide, for purification of water contaminated by pesticides, pharmaceuticals, phenol and other aromatics. The presence of heavy metals in water exhibits a variety of harmful effects on the living organisms in polluted ecosystems. The removal of heavy metals from water includes the following procedures: chemical precipitation, coagulation/flocculation, membrane processes, ion exchange, adsorption, electrochemical precipitation, etc. [31,32]. However, the application of composite materials in the controlling of pollutants in the environment and drinking water is significant [33,34], as described in further text.

The use of zeolites, natural or synthetic ones in waste water treatments is highly limited due to low adsorption capacity in the case of former and relatively small grain size in latter. Modification of natural or synthetic zeolites toward composite material which would satisfy both essential properties is a challenging task. Tailoring synthetic zeolite resulted in a composite porous host supporting microcrystalline active phase of vermiculite matrix [35]. The vermiculite-based composite showed the same hydraulic properties as natural clinoptilolite with similar grain size (2-5 mm), while the rate of adsorption and maximal adsorption capacity was improved four times. In other words, cation exchange capacity is increased when compared to natural zeolite with a comparative grain size, ion-exchange kinetics are substantially improved in comparison to natural zeolite, and hydraulic conductivity is considerably higher that synthetic powdered zeolite [35].

The development of new composite material based on use of inorganic polymeric flocculants as a combination of anionic and cationic poly-aluminium chloride (PACl) in one unique polyelectrolyte is proposed [36]. The incorporation of the anionic polyelectrolyte into PACl structure noticeably affects its initial properties (*i.e.* turbidity, Al species distribution, pH and conductivity). Interactions are taking place between Al

species and polyelectrolytes molecules over hydrogen bonding (amino/amidic groups of the polyelectrolyte, and the –OH and –H groups of Al species are involved) and electrostatic forces/interactions. This resulted in new composite material. The main advantage of composite coagulants is lower residual aluminium concentration that remains in the treated sample, and more efficient treatments of waters (organic matter removal) can be realized [36]. Additional benefit is in cost effective process in the absence of specific equipment for handling the polyelectrolyte (ex. pumping system, etc.). Taking into account faster flocculation, increased efficiency and cost effectiveness, such new composite material seems to be promising one.

Porous ceramic composites can be prepared by silver nanoparticles-decoration using a silver nanoparticle colloidal solution and an aminosilane coupling agent [37]. The interaction between the nanoparticles and the ceramics comprises the coordination bonds between the –NH$_2$ group and the silver atoms on the surface of the nanoparticles. The composite can be stored for long periods without losing of nanoparticles, also being highly resistance to ultrasonic irradiation and washing. Such composite has shown high sterilization property as an antibacterial water filter [37]. This low cost composite, bearing in mind commonly available synthesis, simple preparation, the use of cheap and non-toxic reagents in the procedure, may be imposed as a potential solution for widespread use in water treatments.

Ultrafine AgO particles-decorated porous ceramic composites are prepared based on the main ingredient, cristoballite. The results on composite structure show that silver(II)oxide decorated diatomite-based porous ceramic composites possess crystal structure, and are composed of tetragonal cristoballite, monoclinic silver(II)oxide and cubic silver(I)oxide [38]. Such AgO-decorated porous ceramic composites show a strong antimicrobial activity and an algal-inhibition capacity. As the extension time is longer, the antibacterial effects are enhanced up to 99.9% [38].

Actual nanostructured composite materials based on multi-walled carbon nanotubes (MWCNT) and titania exhibited strong interphase structure between MWCNT and titania. This contact and interaction facilitated a homogeneous deposition/coverage of titania over MWCNT [39]. The photo-catalytic activity of the prepared composite materials was tested in the conversion of phenol from model watery solution under UV or visible light. The results showed higher photo-catalytic activity of the composite MWCNT and titania than over mechanical mixture proving an assumption on the existence of the interphase structure effect [39].

Nanocomposite membranes based on silica/titania nanotubes over porous alumina supports membranes were prepared [40]. An inserting of amorphous silica into nanophase titania caused the surpressed of phase transformation from anatase to rutile, and decreased the titania particle size. Good photo-catalytic activity of organic contaminants degradation, and wettability of composite membrane under UV-irradiation, helped to obtain high permeate flux across the composite membrane [40].

8. New alumosilicate based composites chemically modified by coatings/thin layers – Tested in the removal of colloidal and ionic forms of harmful heavy metals from water

Without new materials, there are no new technologies. Having in mind this fact, electrochemically active and structurally modified composites were obtained through microalloying and certain metals hydroxides layering, starting from bentonite as alumosilicate precursor. The composites have prognosed electrochemical, ion-exchanging and adsorption properties, as very sensitive structural and surface properties of materials. After the series of experiments, including composites interaction with synthetic waters, the obtained results are presented, analyzed and then systematized in the form of appropriate models of interactions.

8.1. Alumosilicate composite ceramic microalloyed by Sn for the removal of ionic and colloidal forms of Mn

Usually, manganese does not present a health hazard in the household water supply. However, it can affect the flavor and color of water because it typically causes brownish-black staining of laundry, dishes and glassware [32]. Although manganese is one of the elements that are at least toxic, concentrations of manganese much higher than the maximum allowed concentration during long-term exposure can cause health damage. A number of known procedures for the manganese removal are not suitable for an elimination of its all chemical species due to reversible release of manganese into water systems. Therefore, some of these used procedures are at the edge of techno-economical viability. In order to remove ionic and colloidal forms of manganese, a new aluminosilicate-based ceramic composite with defined electrochemical activity was synthesized [41]. Synthesis procedure of the composite material consists of two phases. Firstly, composite particles were synthesized by applying Al/Sn oxide coating on the bentonite particles in an aqueous suspension. In the second phase, aluminium powder was added to the previously obtained plastic mass and after shaping in the form of spheres 1 cm in diameter and drying, sintering was performed at 900°C. Fig. 1 a), b) and c) presents the microstructure of composite by using different magnifications.
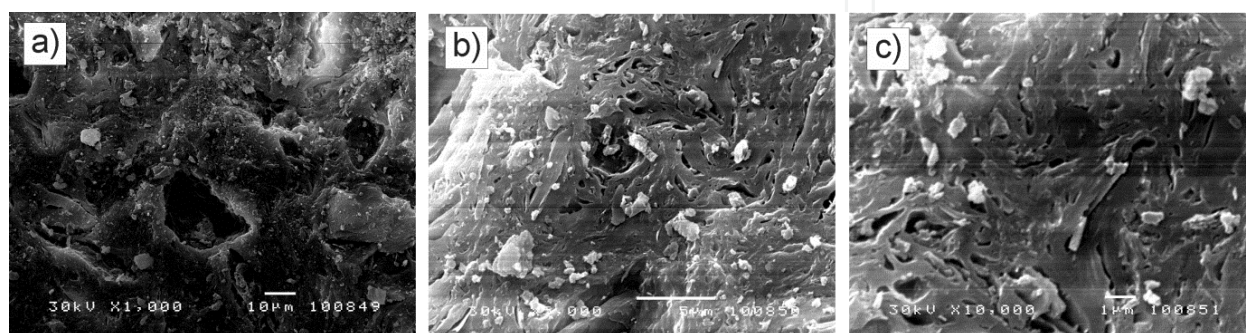

Figure 1. SEM images of the composite recorded at: a) low, b) medium and b) high magnifications.

During sintering a microalloying of composite by Sn occurred causing crystal grain surface layer amorphization and a creation of non-stoichiometric phases of Al_2O_3 with a metal excess [42,43]. In this way, microalloying causes electrochemical activity, which manifests itself in contact with the aqueous solutions of electrolytes and harmful substances in water. Therefore, the ceramics is unstable in contact with water and susceptible to corrosion because surface electrochemical processes taking place. The composite influence redox properties of water and electrochemically interacts with ionic and colloidal forms of manganese in synthetic water systems.

Alumosilicate matrix, whose particles are coated with Al/Sn oxides, was filled with a metal phase which is mostly aluminum with a small quantity of tin as a microalloying component. During the thermal treatment, liquid aluminium simultaneously reacts and penetrates the ceramics preform, resulting in metal/ceramic composite, where the all phases are interpenetrated forming a porous structure. In fact, the reduction of tin(II) occurred according to the following reaction:

$$2Al + 3SnO \rightarrow Al_2O_3 + 3Sn \tag{2}$$

The first reaction step is the reduction of Sn(II) to elemental Sn and its dispersion from the ceramics into the melt. Therefore, during the reaction, Sn is liberated into the liquid metal and diffuses towards the Al source. Moreover, oxygen partial pressure within the composite, at the $Al-Al_2O_3$ interface, can be estimated on the basis of thermodynamic parameters and calculated using the following equation [44]:

$$\Delta G° = RTlnPO_2 \tag{3}$$

The standard free energy of the reaction:

$$4/3Al + O_2 \rightarrow 2/3Al_2O_3 \tag{4}$$

at 900°C, given by Ellingham diagram [44] is -869 KJ/mol, and corresponding oxygen partial pressure: $PO_2 = 2.02 \cdot 10^{-39}$ Pa. Therefore, this low oxygen partial pressure during sintering provides reducing environment and the formation of nonstoichiometric oxide phases, with the metal excess, or with vacancies in oxygen sublattice. Nevertheless, Al_2O_3 belongs to the oxides of stoichiometric composition or with a negligible deviation from stoichiometry, it can occur as an amorphous and nonstoichiometric oxide with a metal excess during oxidation of aluminium. Common nonstoichiometric reactions occur at low oxygen partial pressures when one of the components (oxygen in this case) leaves the crystal [45,42]. A corresponding defect reaction is [45]:

(oxygen in this case) leaves the crystal [45,42]. A corresponding defect reaction is [45]:

$$O_O^x \rightleftarrows \frac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2e^{'} \tag{5}$$

As the oxygen atom escapes, an oxygen vacancy ($V_O^{\bullet\bullet}$) is created. Taking in mind that the oxygen is to be presented in neutral form, two resulting electrons would be easily excited into the conduction band.

Al–Sn alloys show a great activity compared to the thermodynamic Al^{3+}/Al potential of −1.66V vs. NHE, which stands for a pure aluminium. The activation is manifested by a shifting of the pitting potential in the negative direction and significant reducing of the passive potential region [43,46]. The addition of microalloying Sn to aluminium produced a considerable shift of the open circuit potential (OCP) in the negative direction [46].

During the process of composite ceramics sintering, significant changes in the structure of alumosilicate matrix were occurred. Namely, the polycrystaline alumosilicate matrix with amorphised grain and sub-grain boundary were obtained, where a main role possesses metallic aluminum itself, then a microalloyed tin and nonstoichiometric excess of these elements in ceramics, creating macro-, meso- and micro- pores with the reduced mobility of grain boundaries and termination of grain growth [47]. Aluminum and tin in conjunction with other admixtures present in composite ceramics cause drastic changes in the structure-sensitive properties and electrochemical activity. An active composite ceramics in contact with synthetic water containing manganese reduce and deposit the manganese in the macro-, meso- and micro- pores (eq. 6). Electrochemical activity is provided by electrochemical potential of Al atoms and free electrons that participate in redox processes.

$$2Al + 3Mn^{2+} \rightarrow 2Al^{3+} + 3Mn \tag{6}$$

The deposited manganese on microcathode parts of the structure can further form separate clusters and the adsorption layer [48,49]. Reduction processes take place until the Al^{3+} ions continue to solvate themselves in water. A part of Al^{3+} ions reacts with OH^- ions giving insoluble $Al(OH)_3$.

8.1.1. Interaction of composite material with ionic and colloidal forms of Mn in synthetic water

Interaction of the composite material with water manifests itself as decreasing in the redox potential of water, as shown in Fig. 2. This confirms the fact that the composite is electrochemically active in contact with water. During the interaction with water, aluminium from the composite is electrochemically dissolved into water providing electrons which can participate in the number of redox reactions of water yielding reduced species (molecules, ions and radicals) such as H_2, $OH^\bullet$, etc. [47].

TDS value of distilled water immediately after contact with ceramics increases. It seems that increasing the TDS value is due to dissolution of Al^{3+}, Mg^{2+}, Na^+, SiO_3^{2-} from the bentonite based composite. Al^{3+} and SiO_3^{2-} ions are subjected to hydrolysis and polymerization reactions which are followed by spontaneous coagulation-flocculation processes and appearance of sludge after a prolonged period of time.

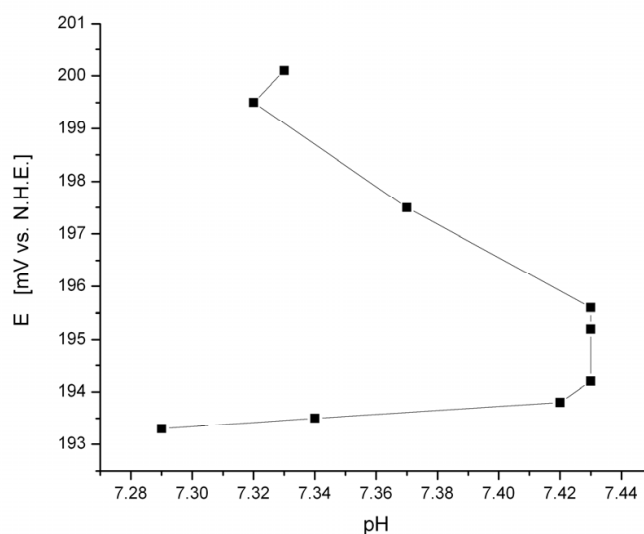A reduction of manganese concentration in synthetic waters is shown in Fig. 3.

Figure 2. Redox potential of water dependence on pH during interaction of the composite with distilled water.
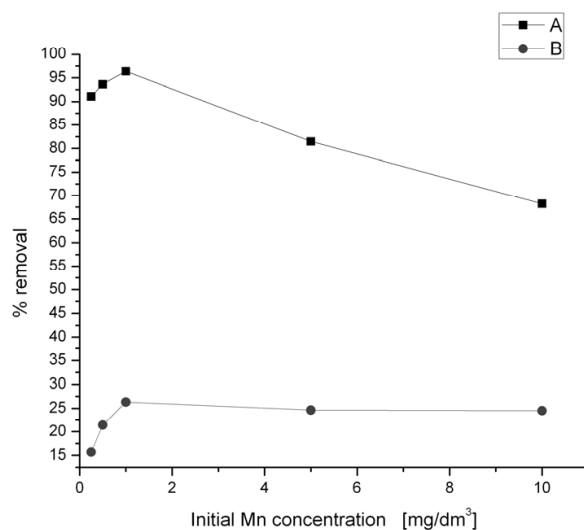

Figure 3. Percentage removal of Mn^{2+} (A) and colloidal MnO_2 (B) from synthetic waters (the composite dosage, 2 g/dm^3; contacting time, 20 min; initial Mn concentrations in range 0.25 – 10 mg/dm^3; initial pH 5.75 ± 0.1; temperature, 20 ± 0.5°C).

Average initial pH of the synthetic waters was 5.75. After 20 min of contact with the composite material average pH was 6.70.

During the interactions of composite with synthetic waters, the colloidal MnO_2 was removed to a lesser degree than Mn^{2+}. The authors imposed that colloidal manganese possesses the following structure of micelles:

$$\{m[MnO_2]nSO_4^{2-} \, 2(n\text{-}x)K^+\}2xK^+ \qquad (7)$$
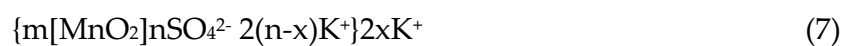
Potential-determining ions in the structure of micelles are SO_4^{2-}. They are primarily adsorbed on MnO_2 and responsible for the stability of colloids. Therefore, it is clear that the reduction of manganese is more difficult and there is an electrostatic repulsion between colloidal particles and a composite with dominantly negatively charged surface sites. Thus, the removal efficiency of colloidal manganese is significantly lower compared with the ionic form of Mn^{+2}. During the electrochemical interactions of synthetic water containing Mn^{2+} and colloidal MnO_2 with the composite material, transferring of Al^{3+} ions in a solution increases the TDS value, as shown in Table 1.

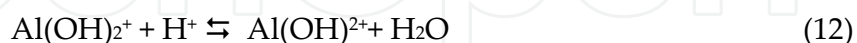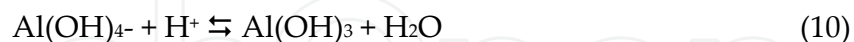| $C_0(Mn)$ mg/dm^3	TDS (mg/dm^3)	pH	$C(Mn)$ mg/dm^3	TDS (mg/dm^3)	pH
Before Mn^{2+} synthetic water treatment			After Mn^{2+} synthetic water treatment		
0.25	3	5.75	0.0223	17	6.65
0.50	7	5.73	0.0318	21	6.71
1.0	10	5.71	0.0363	25	6.72
5.0	14	5.70	0.9271	29	6.70
10.0	28	5.76	3.9773	39	6.58
Before colloidal MnO_2 synthetic water treatment			After colloidal MnO_2 synthetic water treatment		
0.25	3	5.82	0.2108	18	6.73
0.50	6	5.75	0.3928	22	6.71
1.0	11	5.71	0.7366	25	6.72
5.0	14	5.72	3.768	29	6.75
10.0	28	5.75	7.549	39	6.67

Table 1. The results of synthetic waters analysis before and after treatment with composite material.

The initial dissolution of the Al based alloys introduces both aluminium and alloying ions into the solution, and then the reposition of microalloying tin onto active sites at surface occurs [46], so it was not detected by ICP-OES analysis.

Aluminium ions generated during electrochemical processes of manganese removal may form monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$. During the time, these monomers have tendency to polymerize in the pH range 4–7 which results in oversaturation and formation of amorphous hydroxide precipitate according to complex precipitation kinetics. Many polymeric species such as $Al_6(OH)_{15}^{+3}$, $Al_7(OH)_{17}^{+4}$, $Al_8(OH)_{20}^{+4}$, $Al_{13}O_4(OH)_{24}^{+7}$, $Al_{13}(OH)_{34}^{+5}$ have been reported [50]. Average concentration of aluminium, immediately after 20 min of composite interaction with Mn^{2+} synthetic waters, was 0.2131 mg/dm^3 and included all mentioned monomeric and polymeric species which were not coagulated. After a prolonged period of time concentration of aluminum has a tendency to decrease reaching values that are below 0.1 mg/dm^3, due to precipitation of $Al(OH)_3$ sludge.

The increase in the pH during the experiments can be explained in terms of the electrochemical and the chemical reactions that take place in the system composite-synthetic

water. Water reduction at cathodic parts of composite (eq. 8), the electrochemical dissolution of aluminum (eq. 9) and protolytic reactions (eq. 10-14) increase the pH value [51].

$$H_2O + e^- \leftrightarrows 1/2 H_2 + OH^- \tag{8}$$

$$2Al + 6H_2O \leftrightarrows 2Al^{3+} + 3H_2 + 6\ OH^- \tag{9}$$

$$Al(OH)_4^- + H^+ \leftrightarrows Al(OH)_3 + H_2O \tag{10}$$

$$Al(OH)_3 + H^+ \leftrightarrows Al(OH)_2^+ + H_2O \tag{11}$$

$$Al(OH)_2^+ + H^+ \leftrightarrows Al(OH)^{2+} + H_2O \tag{12}$$

$$Al(OH)^{2+} + H^+ \leftrightarrows Al^{3+} + H_2O \tag{13}$$

$$Al(OH)_3(s) \leftrightarrows Al^{3+} + 3OH^- \tag{14}$$

8.2. Bentonite modified by mixed Fe, Mg (hydr)oxides coatings for the removal of ionic and colloidal forms of Pb(II)

Lead (Pb) is heavy metal which presents one of the major environmental pollutants due to its hazardous nature. It diffuses into water and the environment through effluents from lead smelters as well as from battery, paper, pulp and ammunition industries. Scientists established that lead is nonessential for plants and animals, while for humans it is a cumulative poison which can cause damage to the brain, red blood cells and kidneys [52].

In this subchapter, a cheap and effective composite material as a potentially attractive adsorbent for the treatment of Pb(II) contaminated water sources has been described. The procedure for obtaining a bentonite based composite involves the application of mixed Fe and Mg hydroxides coatings onto bentonite particles (0.375 mmol Fe and 0.125 mmol Mg per gram of bentonite) in aqueous suspension and subsequent thermal treatment of the solid phase at 498 K [53]. Bearing in mind layered structure of montmorillonite, the quite limited extent of isomorphous substitution of Mg for Fe in iron (hidr)oxides and significant differences in acid-base surface properties between these two (hydr)oxides, formation of heterogeneous coatings onto bentonite and specific structure of obtained composite have been achieved [54]. Different adsorption sites on such heterogeneous surface provide efficient removal of numerous chemical species of Pb(II) over a wide pH range.

The structural changes of montmorillonite during composite synthesis are mainly reflected in the reduction of d_{001} diffraction peak intensity in X-ray diffractograms and its shifting towards the higher values of 2θ. Moreover, it can be observed that the peak is broadened suggesting that the distance between the layers is non-uniform with disordered and partially delaminated structure. The crystallographic spacing d_{001} of montmorillonite in the native bentonite and the composite, computed by using Bragg's equation ($n\lambda = 2d \sin \theta$), is 1.54 nm and 1.28 nm, respectively. These changes in the structure took place because the d-spacing is very sensitive to the type of interlamellar cations, and the degree of their hydration [55].

The XRD patterns of the composite and starting (native) bentonite are presented in Fig. 4a and b, respectively.
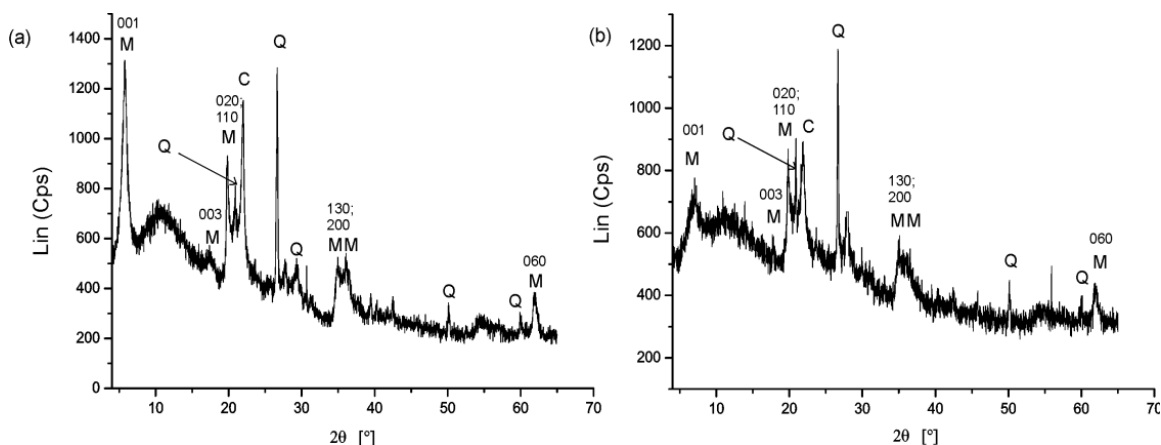

Figure 4. X-ray diffractograms of (a) composite and (b) native bentonite

SEM micrographs (Fig. 5 a, b and c) show that bentonite and composite are composed of laminar particles arranged in layered manner, forming the aggregates with diameters up to 50 μm.
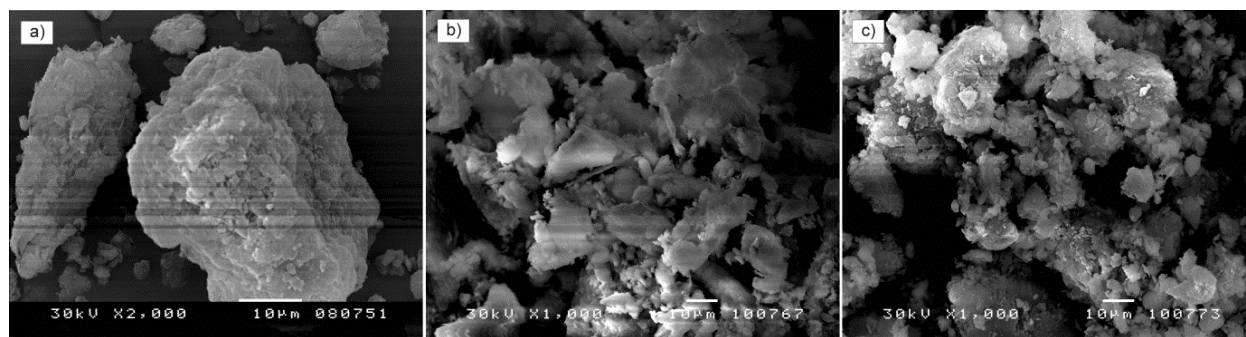

Figure 5. (a) SEM of synthesized composite, (b) SEM of composite after interaction with Pb(II) solution and (c) surface morphology of the native bentonite

No significant changes in the microstructure of composite occurred during the interaction with the aqueous solution of Pb(II).

Despite a thorough washing process, a large amount of NO_3^- is retained in the composite. A vibration mode at ca. 1389 cm^{-1} in FTIR spectrum confirms the NO_3^- stretching which indicates that some positive charged sites exist on the surface of composite and that they are counterbalanced by the NO_3^- which can be exchanged by other anions [53]. In addition, the formation of poorly crystallized magnesium hydroxonitrate in pH range 9-11 [56,57], where Fe/Mg coprecipitation was performed over bentonite particles, is very likely.

8.2.1. Specific surface area determined by N₂ adsorption/desorption using BET equation

The Fig. 6. shows the comparative nitrogen adsorption-desorption isotherms of native bentonite and composite.
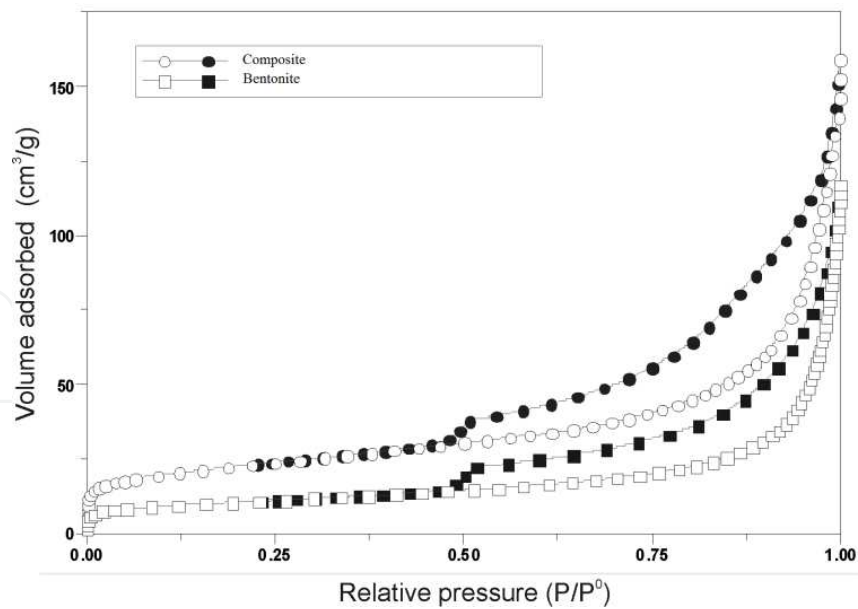
Figure 6. Nitrogen adsorption-desorption isotherms of native bentonite and composite.

The isotherms can be assigned to Type II isotherms, corresponding to non-porous or macroporous adsorbents. The hysteresis loops of Type H3 in the IUPAC classification occur at $p/p^0 > 0.5$, which is not inside the typical BET range. Furthermore, hysteresis loops of these isotherms indicate that they were given by either slit-shaped pores or, as in the present case, assemblages of platy particles of montmorillonite. Porous structure parameters are summarized in Table 2.

Sample	S_{BET} (m²/g)	Median mesopore diameter (nm)	Cumulative mesopore area (m²/g)	Cumulative mesopore volume (cm³/g)	Micropore volume (cm³/g)
Bentonite	37.865	13.629	53.329	0.1202	0.0153
Composite	80.385	11.021	82.675	0.1716	0.0316

Table 2. Specific surface area and porosity of native bentonite and composite, determined by applying BET, BJH and D-R equation to N₂ adsorption at 77 K

Compared to native bentonite, during the composite synthesis additional meso- and micropores were generated. Pore volumes (Gurvich) at p/p^0 0.999 for bentonite and composite are 0.180 cm³/g and 0.243 cm³/g, respectively. It was found that isotherms gave linear BET plots from p/p^0 0.03 to 0.21 for bentonite and from 0.03 to 0.19 for composite.

The composite has the specific surface area that is twice the size compared to the surface area of the native bentonite. This can be explained by the structural changes that occurred during the chemical and thermal modification of the native bentonite. The structural changes include delamination as well as the decrease of the distance between the layers of montmorillonite particles, because the interlayer water was lost under heating. The higher surface area of composite mainly results from the interparticle spaces generated by the

three-dimensional co-aggregation of magnesium polyoxocations, iron oxide clusters and plate particles of montmorillonite. Macro- and mesopores arose from particle-to-particle interactions, while micropores were generated in the interlayer spaces of clay minerals due to irregular stacking of layers of different lateral dimensions [58].It is apparent that the changes of montmorillonite structure are responsible for the creation of new pore structure in the composite, which is then stabilized by the thermal treatment with the removal of H_2O molecules. The changes that involve partial dehydroxylation and cationic dehydration are brought about by thermal activation and they lead to various forms of cross-linking between oxides and smectite framework. As a result, composite does not swell and can be easily separated from water by filtration or centrifugation. There is a wide pore size distribution which supports disordered structure consisting of the delaminated parts with mesoporosity and the layered parts with microporosity.

The pH of the Pb(II) solution plays an important role in the adsorption process, influencing not only the surface charge of the adsorbent and the dissociation of functional groups on the active sites of the adsorbent but also the solution Pb(II) chemistry. The adsorption of Pb(II) on the composite decreased when pH decreased as shown in Fig. 7.
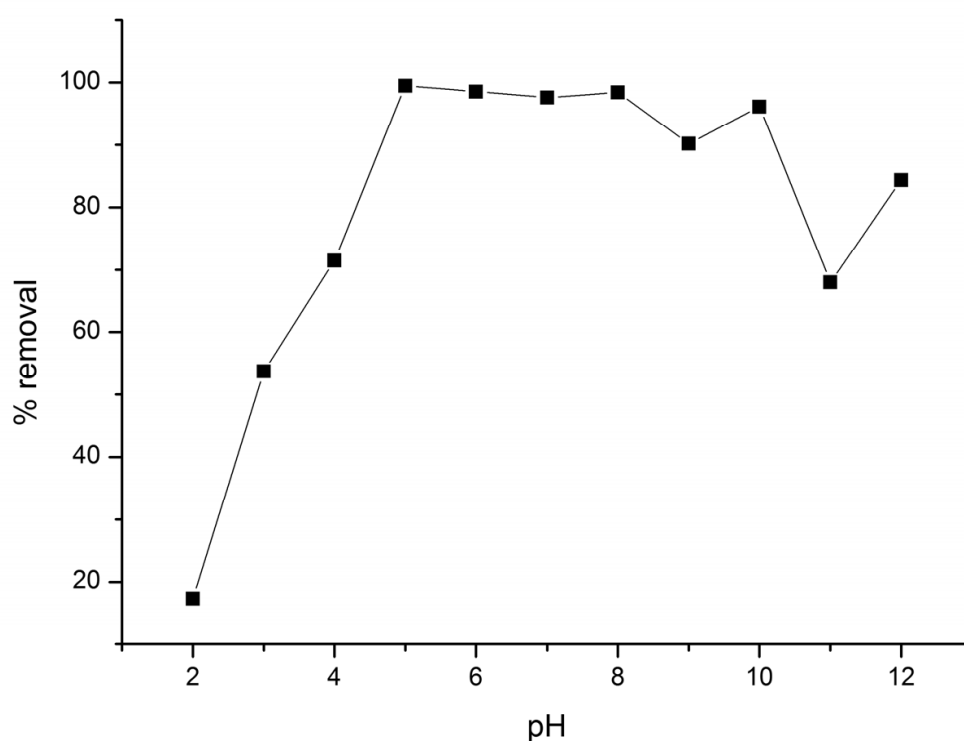

Figure 7. Effect of pH on adsorption of Pb(II) onto composite

The adsorptive decrease at pH below 5 was caused by the competition between H^+ and Pb^{2+} for the negatively charged surface sites. Maximum retention is in the pH range 5-10. The main Pb(II) species in the pH range 6.5-10 are $Pb(OH)^+$ and $Pb(OH)_2$ which can easily form colloidal micelles characterized with the following imposed structure:

$$\{m[Pb(OH)_2]nPb(OH)^+\cdot(n-x)NO_3^-\}xNO_3^- \tag{15}$$
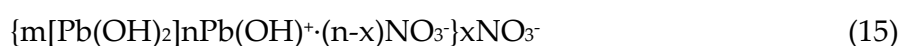
The potential – determining ion is Pb(OH)$^+$ and that is the reason for the positive ZP of colloidal Pb(II) at the pH below 10 [59,60]. Therefore, colloidal micelles were easily attracted by the negatively charged composite surface. Particle size of colloidal Pb(II) at pH 7±0.1 was determined to be 268.7 ± 16.7 nm. At the pH range of 10-12 the predominant Pb(II) species are Pb(OH)$_2$ and Pb(OH)$_3^-$ which give rise to the formation of negatively charged colloidal micelles with the following structure:

$$\{m[Pb(OH)_2]nPb(OH)_3^- \cdot (n-x)Na^+\}xNa^+ \tag{16}$$
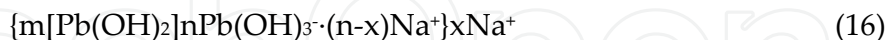
ZP values for Pb(II) colloidal solutions at pH 11.8 were - 50.7±3.6 mV with particle size of 252.7±28.2 nm. Having in mind surface heterogeneity of the composite and high point of zero charge value of Mg(OH)$_2$ (between pH 12 and pH 13) [61], negative ions and particles can be adsorbed on the positively charged surface sites at pH 10-12. Removal efficiency of Pb(OH)$_3^-$ was higher than negatively charged colloids, probably because the ionic species were involved in the process of ion exchange and chemisorption, while colloidal micelles could be bound to the surface dominantly by electrostatic forces.

8.3. Bentonite based composite coated with immobilized thin layer of organic matter

Synthesis of bentonite based composite material, described in this section, was carried out by applying thin coatings of natural organic matter, obtained by alkaline extraction from peat, mostly comprised of humic acids [62]. Humic acids have high complexing ability with various heavy metal ions, but it is difficult to use them as the sorbent because of their high solubility in water. However, they form stabile complexes with the inorganic ingredients of bentonite (montmorillonite, quartz, oxides, etc.) and can be additionally insolubilized and immobilized by heating at 350°C. After immobilization, humic acids represent an important sorbent for heavy metals, pesticides and other harmful ingredients from water. Humic acid are insolubilized by condensation of carboxylic and phenolic hydroxyl groups. Therefore, the aim was to remove manganese from aqueous solutions by treating it with synthesized composite as well as to study and explain the mechanism of composite interaction with manganese aqueous solutions. The composite does not release significant quantity of organic matter in water because it is tightly bonded to bentonite surface [63-65]. The degree of manganese removal was more than 94% at a range of initial manganese concentrations from 0.250 to 10 mg/l.

The result of conductometric titration is given in Fig. 8. Equivalence point was located at the intercept of the first and second linear part of the titration curve. The value of the total acidic group content is calculated to be 215.18 μmol/g.

The experimental data of manganese adsorption onto composite are very well fitted by the Freundlich isotherm model (Fig. 9.) with a very high correlation coefficient value of 0.9948. The good agreement of experimental data with the Freundlich model indicates that there are several types of adsorption sites on the surface of the composite. The amount of adsorbed Mn(II) increases rapidly in the first region of adsorption isotherm and then the slope of

isotherm gradually decreases in the second region. The adsorption capacity of composite is 11.86 mg/g, at an equilibrium manganese concentration of 16.28 mg/l.
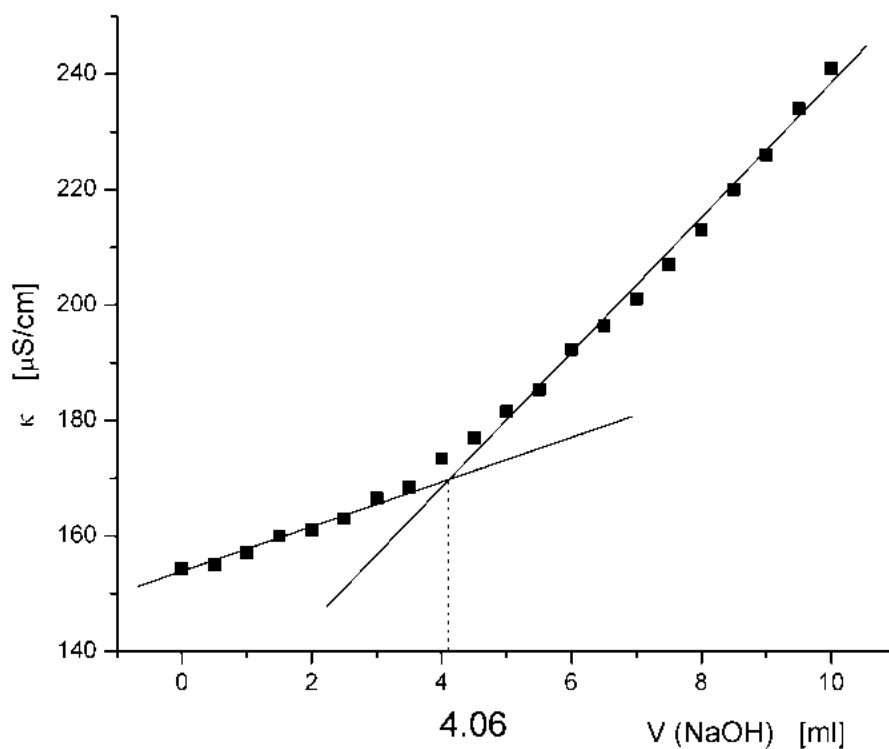

Figure 8. The conductometric titration of composite suspension (1 g in 250 ml of 1mM NaCl solution as background electrolyte) with 0.053 M NaOH.

After the treatment of model water with composite for the period of 20 min, the following results were obtained (Table 3).

Before water treatment			After water treatment			
C₀(Mn)mg/l	pH	Conductivity µS/cm	pH	Conductivity µS/cm	C(Mn) mg/l	%Mn Adsorption
0	6.43	8.01	6.67	11.43	0	0
0.250	6.37	9.57	7.11	13.76	0.0030	98.8
0.490	6.32	10.67	7.15	15.31	0.0039	99.2
1.0	6.30	14.67	7.12	31.10	0.0090	99.1
2.5	6.20	20.70	6.96	37.20	0.0187	99.25
5.0	6.19	32.80	6.83	49.40	0.0646	98.71
10.0	6.16	55.30	6.70	68.90	0.5314	94.69

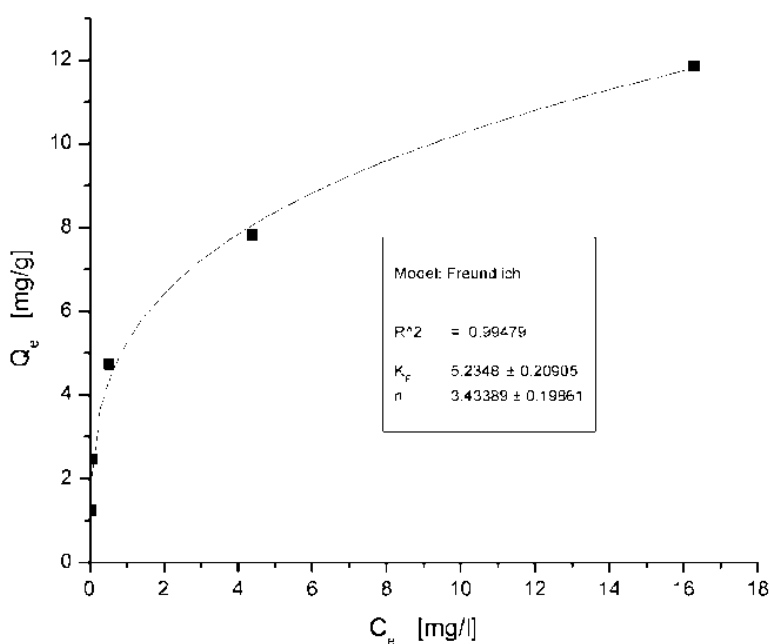**Table 3.** The results of water analysis before and after treatment with composite

Figure 9. Freundlich adsorption isotherm for manganese adsorption onto composite.
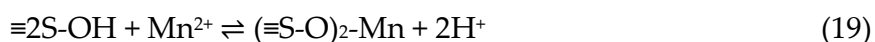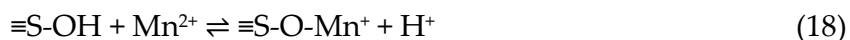
During the thermal treatment in nitrogen atmosphere at 350 °C, the condensation of carboxyl and adjacent alcohol and phenol groups occurs. In this way the solubility of organic matter immobilized on bentonite matrix surface decreases [65]. Moreover, a part of carboxyl groups is decomposed by decarboxylation reaction, releasing CO_2 and CO. However, despite of this, a part of oxygen functional groups remains on the surface, and these groups act as sites that bind bivalent manganese forming inner-sphere complexes.

Besides organic functional groups, there are also Si-OH and Al-OH groups on the sites of crystal grain breaks, as well as permanent negative charge due to isomorphic substitution in clay minerals. They all contribute to the reduction of manganese concentration in the aqueous solution. Manganese retention by the formation of outer-sphere complexes, including ion exchange, can be showed by an Eq. (17) [66].

$$(\equiv S\text{-}O^-)_2...C^{n+}_{3-n} + Mn^{2+} \rightleftharpoons (\equiv S\text{-}O^-)_2...Mn^{2+} + (3\text{-}n)\ C^{n+} \tag{17}$$

in which C represents the cation that is exchanged.

The formation of inner-sphere complexes is represented by the Eqs. (18) and (19) and involves the release of hydrogen ions and the change of solution pH.

$$\equiv S\text{-}OH + Mn^{2+} \rightleftharpoons \equiv S\text{-}O\text{-}Mn^+ + H^+ \tag{18}$$

$$\equiv 2S\text{-}OH + Mn^{2+} \rightleftharpoons (\equiv S\text{-}O)_2\text{-}Mn + 2H^+ \tag{19}$$

According to these equations, it can be concluded that the pH value of the solutions decrease after the treatment. However, an opposite phenomenon can be experimentally observed (Table 3). The explanation for it is that hydrogen ions which are released during manganese retention participate in the protonation of surface groups:

$$\equiv S\text{-}OH + H^+ \rightleftharpoons \equiv S\text{-}OH_2^+ \tag{20}$$

$$\equiv S\text{-}O^- + H^+ \rightleftharpoons \equiv S\text{-}OH \tag{21}$$

Therefore, the pH value of the Mn^{2+} aqueous solutions after treatment with composite had a higher value than the initial pH. This indicates that more hydrogen ions are bound to the surface than released by manganese binding. Namely, the composite exhibits amphoteric character due to the surface sites that act either as proton acceptors or as proton donors.

Organic matter decreases the PZC value of bentonite and neutralizes positive electric charge that comes from interlaminated cations, thus increasing composite affinity to manganese, even at lower pH values (67). Fig. 10. presents the pH dependence of residual Mn concentration, for the initial Mn concentration of 5 mg/l. The residual concentration of Mn decreases gradually with pH increasing in the range of 3.5-7 and then increases in the range of 7-10, with the apparent minimum at pH 7.
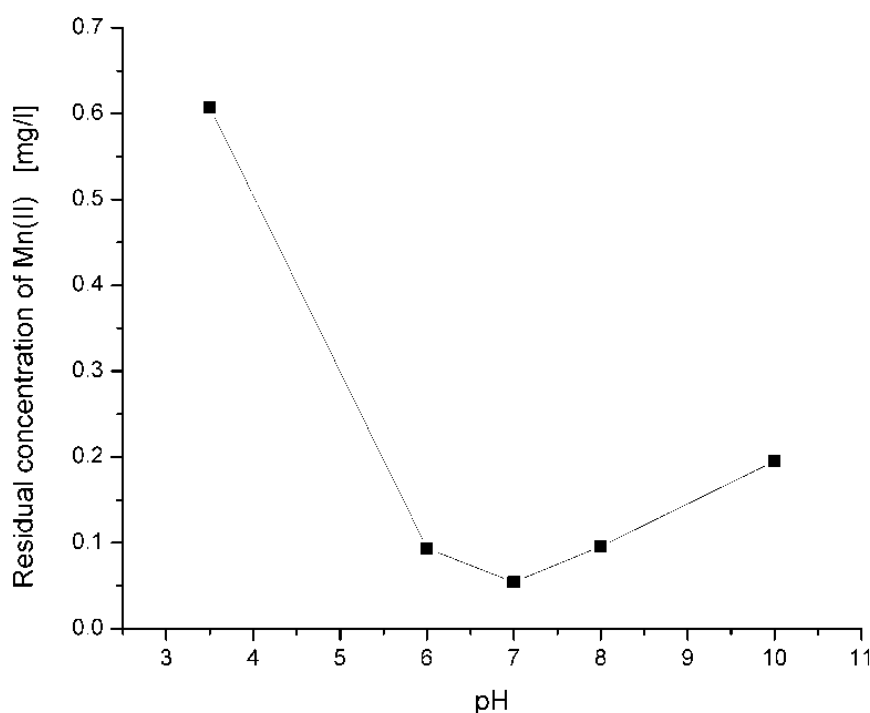

Figure 10. Residual concentration of Mn(II) as a function of model water pH.

The increase of pH value has dual effect on the removal of manganese. The increase of the pH value favours manganese removal due to increase of the number of deprotonated sites that are available for the binding of manganese. However, there is an increase in the solubility of organic matter which has been applied on the bentonite particles. The dissolved organic matter (humic acids) reacts with manganese forming complexes which bear a negative charge and have a weaker binding affinity for the composite surface than Mn^{2+}. Fig 10. indicates two opposite effects of the pH on manganese removal. The pH dependence of released organic matter (expressed as permanganate number) and turbidity (NTU) of solutions are shown in Fig. 11.
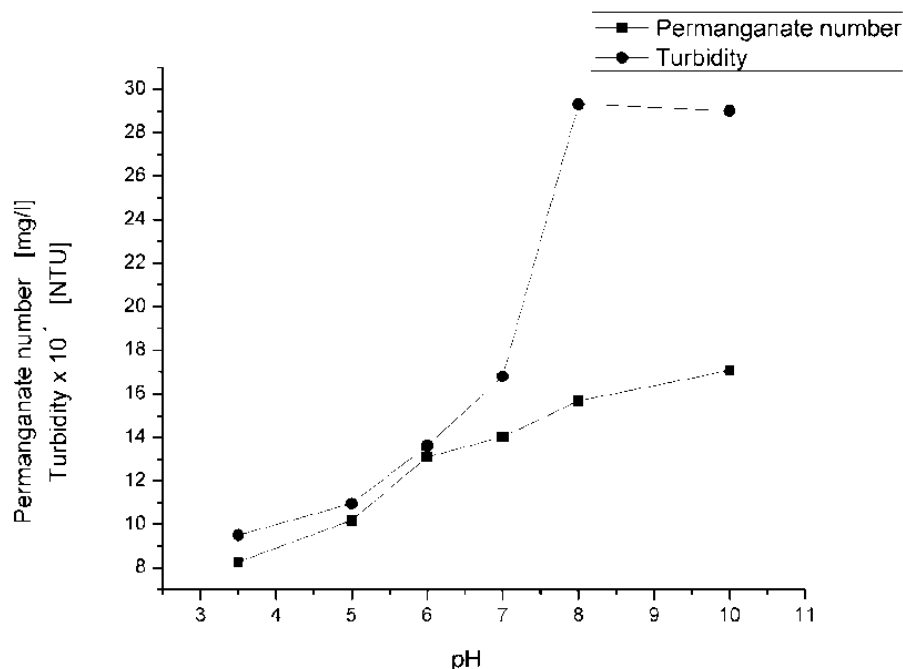
Figure 11. Premanganate number and turbidity of filtrate as function of pH (0.2 g of composite and 100 ml of 1mM Na$_2$SO$_4$ as background electrolyte).

The released organic matter contributes to the increased turbidity at higher pH values.

9. Summary

The widespread industrial areas where nanocomposites can be applied are primary and conversion industry, modern coating technologies, constructional regions, and environmental (water, air) purification. In addition to the dominant use of composites as structural elements, important application of composite materials is in the water purification technologies. In this field of application, composites usually have the role of adsorbent, electrochemically active materials, catalysts, photocatalysts etc.

Bentonite is a natural and colloidal alumosilicate with particle size less than 10 μm, which is effectively used as sorbent for heavy metals and other inorganic and organic pollutants from water. Due to its positive textural properties and high specific surface area it can be used as low-cost matrix for synthesis of adsorbents or electrochemically active composite materials for the removal of pollutants in ionic and colloidal form from water. In this respect, three new/modified bentonite based composite materials have been synthetised and characterized.

Coated or composite particles are composed of solid phase covered with thinner or thicker layer of another material. These coatings - layers covering the surface of matrix are important for several reasons. In such way, the surface and textural characteristics of the initial solid phase are modified and sintering conditions can be better controlled. An important factor in achieving the desired microstructure of ceramics is sintering procedure that includes rather complex processes. A considerable influence on sintering has been exhibited by an addition of microalloying components, which significantly determined a

microstructure and resulted properties of ceramics. The presence of small amounts of impurities in the starting material can vastly influence their mechanical, optical, electrical, color, diffusive, and dielectric properties of alumosilicate matrix. In summary, the process of diffusion mass transport in ceramic crystal regions are affected by temperature, oxygen partial pressure and concentration of impurities. A procedure for the removal of manganese in ionic (Mn^{2+}) and colloidal (MnO_2) forms from synthetic waters, by reduction and adsorption processes on electrochemically active alumosilicate ceramics based composite material has been described. Synthesis procedure of the composite material consists of two phases. Firstly, composite particles were synthesized by applying Al/Sn oxide coating onto the bentonite particles in an aqueous suspension. In the second phase, aluminium powder is added to the previously obtained plastic mass and after shaping in the form of spheres 1 cm in diameter and drying, sintering was performed at 900°C. Elemental tin, resulting from the reduction of Sn^{2+}-ion, comes into contact with liquid aluminum in the pores of the matrix performing aluminum microalloying and activation. Moreover, due to a low partial pressure of oxygen, nonstoichiometric oxides with metal excess are obtained, and they play an important role in the electrochemical activity of the composite material. In accordance with this, a redox potential of water is changed in contact with composite.

Another effective composite material as a potentially attractive adsorbent for the treatment of Pb(II) contaminated water sources has been synthesized by coating of bentonite with mixed iron and magnesium (hydr)oxides. The procedure for obtaining a bentonite based composite involves the application of mixed Fe and Mg hydroxides coatings onto bentonite particles in aqueous suspension and subsequent thermal treatment of the solid phase at 225ºC. Formation of heterogeneous coatings on bentonite results in changes of bentonite acid-based properties, high specific surface area and positive adsorption characteristics. Different adsorption sites on such heterogeneous surface provide an efficient removal of numerous chemical species of Pb(II) (ionic and colloidal) over a wide pH range.

Third bentonite based composite material was obtained by applying thin coatings of natural organic matter, extracted from a peat, mostly based on humic acids. Humic acids are known due to high complexing ability to various heavy metal ions, but it is difficult to use them directly as the sorbent because of their high solubility in water. However, they form stable complexes with the inorganic ingredients of bentonite (montmorillonite, quartz, oxides, etc.) and can be successfully insolubilized and immobilized by heating at 350°C. After immobilization, humic acids represent an important sorbent for heavy metals, pesticides and other harmful ingredients from water. Humic acid are insolubilized by condensation of carboxylic and phenolic hydroxyl groups. The composite such obtained can be effectively used as the sorbent for heavy metals.

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