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Polymer Nanocomposite Hydrogels for Water Purification

Manja Kurecic and Majda Sfiligoj Smole

Additional information is available at the end of the chapter

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1. Introduction

Contamination of water, due to the discharge of untreated or partially treated industrial wastewaters into the ecosystem, has become a common problem for many countries [1]. In various productions, such as textiles, leather, rubber, paper, plastic and other industries, the dyeing processes are among the most polluting industrial processes because they produce enormous amounts of coloured wastewaters [2-4]. In addition to their colour, some of these dyes may degrade to highly toxic products, potentially carcinogenic, mutagenic and allergenic for exposed organisms even at low concentrations (less than 1 ppm) [5]. They contaminate not only the environment but also traverse through the entire food chain, leading to biomagnifications [6-9]. The removals of such compounds particularly at low concentrations are a difficult problem.

Textile effluents are usually treated by physical and chemical processes such as sorption, oxidation, flocculation, etc. Colour removal by activated carbon, H₂O₂, sodium hyperchlorite and other chemical agents has been widely practiced in the textile industries [10]. Although activated carbon remains the most widely used adsorbent, its relatively high cost restricts its use sometimes. However, in addition to, adsorptive properties and availability are also key criteria when choosing an adsorbent for pollutant removal, thereby encouraging research into materials that are both efficient and cheap. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from agriculture and industry have been proposed by several researchers [11-14]. Considering low cost, abundance, high sorption properties and potential ion-exchange, clay minerals are interesting materials for use as adsorbents, since they can be easily obtained and regenerated [7].

2. Clay minerals

Clays are widely applied in many fields such as polymer nano-composites [15-18], catalysts [19,20], photochemical reaction fields [21], ceramics [22], paper filling and coating [23], sensors and biosensors [24], absorbents, etc. due to their high specific surface area, chemical and mechanical stabilities, and a variety of surface and structural properties [25].

The most-used clays are smectite group which refers to a family of non-metallic clays primarily composed of hydrated sodium calcium aluminium silicate, a group of monoclinic clay-like minerals with general formula of $(\text{Ca,Na,H})(\text{Al,Mg,Fe,Zn})_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$.

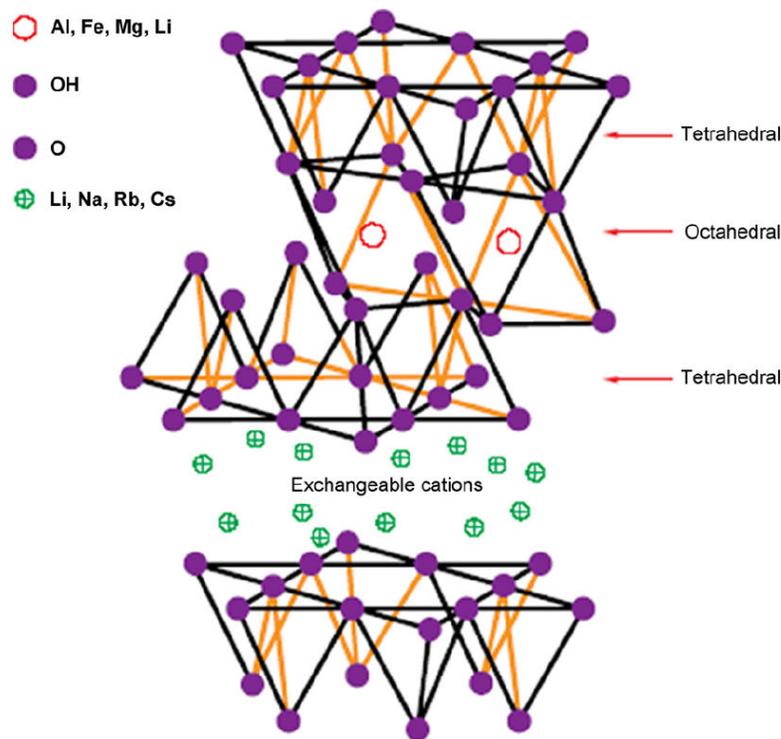


Figure 1. Structure of 2:1 layered silicate [15].

Smectite is a clay mineral having a 2:1 expanding crystal lattice (Figure 1). Its isomorphous substitution gives various types of smectite and causes a net permanent charge balanced by cations in such a manner that water may move between the sheets of the crystal lattice, giving a reversible cation exchange and very plastic properties.

Members of the smectite group include the dioctahedral minerals montmorillonite, beidellite, nontronite, bentonite, and the trioctahedral minerals hectorite (Li-rich), saponite (Mg-rich) and sauconite (Zn-rich). The basic structural unit is a layer consisting of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet. The layers are continuous in the length and width directions, but the bond between layers are weak and have excellent cleavage, allowing water and other molecules to enter between the layers causing expansion in the third direction [15,16,25,26].

In the inner blocks, all corners of silica tetrahedra are connected to adjacent blocks, but in outer blocks some of the corners contain Si atoms bound to hydroxyls (Si-OH). These silanol groups at the external surface of the silicate, are usually accessible to organic species, and act as neutral adsorption sites. In addition to, some isomorphic substitutions occur in the tetrahedral sheet of the lattice of the mineral form leading to negatively charged adsorption sites which are occupied by exchangeable cations [25]. These characteristics make them powerful adsorbents for organic molecules and organic cations. In order to improve the adsorption properties of clay adsorbents also for organic anions, clay surface can be modified. There are many exchangeable cations on the clay surface therefore the cationic surfactants are generally used as modifiers. The characteristics of these so-called organoclays can be changed by variation of surfactant properties, such as alkyl chain length, etc. The surface properties of the clays modified by surfactants alter from organophobic to organophilic, which aids in improving clay adsorption capacities for organic compounds [27]. While crude clay minerals are effective for the adsorption of cations, organo-modified clays may adsorb negative and hydrophobic molecules [25]

2.1. Organically modified clay minerals

Surface modifications of clay minerals have received great attention because it allows the creation of new materials and new applications [28]. Organically modified clay minerals have become essential for development of polymer nanocomposites. Modified clays are also used in other applications such as adsorbents of organic pollutants in soil, water and air; rheological control agents; paints; cosmetics; refractory varnish; thixotropic fluids, etc. Several routes can be employed to modify clays and clay minerals [29]:

- adsorption,
- ion exchange with inorganic cations and organic cations,
- binding of inorganic and organic anions (mainly at the edges),
- grafting of organic compounds, reaction with acids,
- pillaring by different types of poly(hydroxo metal) cations,
- intraparticle and interparticle polymerization,
- dehydroxylation and calcination,
- delamination and reaggregation of smectites,
- lyophilisation,
- ultrasound, and
- plasma.

Ion exchange with alkylammonium ions is well-known and the preferential method to prepare organoclays. Generally, the papers describe the preparation of the organoclays in laboratory scale, with different experimental conditions, clays from several regions and suppliers, and several kinds of organic compounds [28].

The research of intercalation of organic molecules into the interlayer space of clay minerals started in the 1920s, after the introduction of X-ray diffraction in 1913 [28]. Geseking [30] found methylene blue to be very effective in replacing interlayer cations. These results indicated on the possibility of using ammonium ions of the NH_3R^+ , NH_2R_2^+ , NHR_3^+ , and NR_4^+ types for better understanding of the mechanism of cation exchange in clay minerals. Different types of clay minerals were treated with the solution of hydrochlorides or hydroiodides of various amines. The clay minerals adsorbed the organic ions and increased the basal spacing more than those of the same clay minerals saturated with smaller cations such as calcium or hydrogen.

In 1944 MacEwan observed that when montmorillonite was treated with glycerol, a very sharp and intense first-order x-ray diffraction reflexion was obtained, corresponding to the basal spacing of 1.77 nm. The increase of basal spacing was due to the intercalation of glycerol into the interlayer space of the clay mineral. [31].

Studies of interactions between clay minerals and organic compounds have been presented, among others, in [32-34]. Clay-organic complexes of great industrial importance are the organoclays prepared from smectites and quaternary ammonium salts.

2.2. Organically modified clay minerals for dye adsorption

There are more than 100 000 types of dyes commercially available, with over 7×10^5 tons of dyestuff produced annually, which can be classified according to their structure as anionic and cationic. In aqueous solution, anionic dyes carry a net negative charge due to the presence of sulphonate (SO_3^-) groups, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulphur containing groups. [35]

Reactive dyes are extensively used in the textile industry because of their wide variety of colour shades, brilliant colours, and minimal energy consumption [36]. Therefore, considerable amount of research on wastewater treatment has focused on the elimination of these dyes, essentially for three reasons: firstly, reactive dyes represent 20-30% of the total dye market; secondly, large fraction of reactive dyes (10-50%) are wasted during the dyeing process (up to 0,6 – 0,8 g dye/dm³ can be detected in dyestuff effluent); thirdly, conventional wastewater treatment methods, which rely on adsorption and aerobic biodegradation, were found to be inefficient for complete elimination of many reactive dyes. [35]

Comprehensive research activities in the field of dye adsorption onto organically modified clays are directed to different organic modifiers in order to improve and broaden the applications of clay adsorbents [36-38]. The hexadecyltrimethylammonium (HDTMA) bentonite was synthesized by placing alkylammonium cation onto bentonite [38]. Adsorption of several textile dyes such as Everdirect Supra Yellow PG, Everdirect Supra Orange 26 CG, Everdirect Supra Rubine BL, Everdirect Supra Blue 4 BL and Everdirect Supra Red BWS on Na-bentonite and HDTMA-bentonite was investigated. While the Na-bentonite had no affinity for the dyes, the HDTMA-bentonite showed significant adsorption from aqueous solution. Wang et al. has reported that adsorption capacity for Congo Red of modified montmorillonite sharply increases from 31.1 to 299 mg of adsorbate per g of adsorbent with increasing the

numbers of carbon atom of surfactant from 8 to 16 and then decreases with further increasing the number of carbon atom of surfactant from 16 to 18 [27]. He explained that alkyl chains of surfactant intercalate into the montmorillonite galleries and broaden the galleries, which in turn result in an increase in the adsorption. In recent years many reports showed that the surfactant-modified clays displayed higher adsorption capacity than the original clay. Modification of bentonite clay with cetyltrimethylammonium bromide enhanced the rate at which direct dye Benzopurpin 4B is absorbed on Na-bentonite [39]. Zohra et al. explained that increase in adsorption capacity of modified clay is due to the alkyl chains in the interlamellar spaces functioning as organic solvent in portioning and electrostatic attraction with positively organoclay surface and anionic dye molecules. There have also been trials to modify montmorillonite clay with novel Gemini surfactants under microwave irradiation [40]. They have studied the adsorption behavior of methyl orange dye on MMT and three kinds of organo-MMTs modified using Gemini surfactants. All organo-MMTs displayed more excellent adsorption capacities than MMT, and as the amount or the chain length of Gemini surfactants increased, the adsorption capacity of the organo-MMTs was improved. XRD analyses were used in order to confirm the enlargement of interlayer spacing in organo-MMTs which results in higher surface area leading to the stronger adsorption capacity. In addition to, from SEM analysis it was observed that the structure of organo-MMTs was looser, which can facilitate the adsorption of the dyes on organoclays. Based on TGA results, the surface energy of organo-MMT was reduced from hydrophilic to hydrophobic, which is helpful for absorbing the organic methyl orange. With the increase of the amount or the chain length of the Gemini surfactant, the hydrophobicity of the modified MMT was higher, and it facilitated the adsorption of organic contaminants. Özcan et al. have also investigated the effect of pH on the adsorption of Reactive Blue 19 from aqueous solution onto surfactant-modified bentonite [4]. Dodecyltrimethylammonite (DTMA) bromide was used as a cationic surfactant. pH was in the range between 1-9 and it was found that the adsorption decreased with an increase of pH. Batch studies suggest that the high adsorption capacity of DTMA-bentonite in acidic solutions (pH around 1.5) is due to the strong electrostatic interaction between its adsorption site and dye anion.

In several research articles it is indicated that clay derivatives are potentially very promising sorbents for environmental and purification purposes. Although the modification of clays with surfactants increases their cost significantly, the resultant increase in adsorption capacity may still make surfactant-modified clays cost effective. The nano-clay, montmorillonite, and some modified nano-clays were used as sorbents for non-ionic, anionic and cationic dyes [41]. From the sorption differences among the different dye and clay structures, both chemical and morphological, the sorption forces that played important roles were identified. Nano-clays frequently have a sorption capacity of more than 600 mg sorbate per gram of sorbent at a liquor-to-sorbent ratio of 100:1. Furthermore, a sorption of 90% at the initial dye concentration of 6g/L, or 60% based on the weight of sorbent, was observed. This indicates an extremely high dye affinity. This study showed that by modification of the nano-clay MMT, it can easily become an excellent sorbent for anionic, cationic and non-ionic dyes.

Clay minerals are in most cases used as dispersed adsorbents and as such aggravate the removal of adsorbents from clean purified water. Recently, there have been some activities to incorporate clay particles into nanocomposite hydrogels for application in wastewater technologies [42-45]. Incorporation of clay minerals in hydrogel matrix allows better manipulation with adsorbing material since clay minerals are fixed in the matrix.

3. Clay/polymer nanocomposite hydrogels

Hydrogels are 3D dense cross linked polymer network structure, containing hydrophilic and hydrophobic parts in a defined proportion. When placed in aqueous medium, they intensively swell. By swelling they increase their initial volume for several times without either dissolving or considerably changing their shape, because hydrophilic chains contact one to the other by cross-linking [42,46,47]. The response of hydrogel is dependent on the presence of hydrophilic functional groups such as $-OH$, $-COOH$. These groups make the hydrogel hydrophilic and due to the capillary action and the difference in the osmotic pressure, water diffuses into the hydrogel.

Polymerization methods, the presence of functional groups and the nature of cross-linking agents are important parameters that control the swelling ability of hydrogel [43].

Owing to their advantageous properties, such as swellability in water, hydrophilicity, biocompatibility and lack of toxicity, hydrogels have been utilized in a wide range of hygienic, agricultural, medical and pharmaceutical applications and in such applications, water absorbency and water retention properties are essential [46,48]. The most well-established hydrogel applications are superabsorbing hydrogels in diapers and hydrogels for contact-lenses, just to mention few [49-53].

Recently hydrogels have gain particular interest in wastewater treatment due to their high adsorption capacities, especially regeneration abilities and reuse for continuous processes [54]. But pure hydrogels often have some limitations such as low mechanical stability and gel strength. In the initial phase of nanocomposite hydrogels development, various clay minerals were widely added to polymer hydrogel matrix in order to improve weak mechanical stability of hydrogels. Sodium montmorillonite (NaMMT) or attapulgite were used as reinforcing filler in the preparation of hydrogels to improve mechanical properties or swelling ability (55-58). Liang et al. [59] used organically modified montmorillonite to prepare hydrogels that exhibited higher swelling degree and enhanced thermal response compared to conventional poly(N-isopropylacrylamide) (PNIPAM) hydrogels. Hydrogels were also prepared with ionic monomers and montmorillonite [60]. However, the transparency, swelling degree and mechanical property did not improve simultaneously, in particular at relatively high NaMMT loading, because of the poor dispersion of clay mineral particles and structural inhomogeneity of the hydrogel network caused by the crosslinker N,N'-methylene-bis-acrylamide (BIS) [61]. To overcome this problem, a special type of an inorganic-organic thermo-responsive PNIPAM nanocomposite hydrogel was developed by Haraguchi, containing laponite XLG without any chemical crosslinker. The exfoliated laponite particles

acted as multifunctional crosslinker, and the polymer chains were anchored to the particles and entangled to form a network [49,50,53]. According to this mechanism several researches prepared various nanocomposite hydrogels by using laponite as multifunctional crosslinker [56,61]. The resulting hydrogels exhibited not only excellent optical and ultrahigh mechanical properties but also large swelling ratios and rapid shrinking capability [49,50,53,61,62].

Despite of undesired low mechanical properties, which can be improved by introduction of clay minerals in the hydrogel matrix, hydrogels have many predominant properties including low interfacial tension and a variety of functional groups which can trap ionic dyes from wastewater and provide high adsorption capacities [63]. Introduction of clay materials into hydrogel combines improvement of elasticity and permeability of the hydrogels with high ability of the clays to adsorb different substances. Application of low-priced and biodegradable adsorbents is a good tool to minimize the environmental impact caused by dye manufacturing and textile effluents. Consequently, research concerning development of hydrogels with clay particles for adsorbing dyes and metal ions is exponentially increasing [43,42,54,64].

Shirsath et al. synthesized polymer nanocomposite hydrogels using metal hybrid polymer along with clay. Ultrasonic irradiation was used to initiate the emulsion polymerization to form hydrogel through the generation of free radicals. The high shear gradients generated by the acoustic cavitations process help to control the molecular weight of hydrogels formed in aqueous solutions. Ultrasound was found to be an effective method for polymerization of monomers and for the production of hydrogel in the absence of a chemical initiator [43].

3.1. Clay/polymer nanocomposite synthesis

Hydrogels are usually crosslinked during polymerization via condensation polymerization or free radical polymerization (thermal polymerization, radiation polymerization, photopolymerization or plasma polymerization) [65-67]. Photo-polymerization, in addition to its environmental-friendly aspects, offers a number of advantages, such as ambient temperature operations, location and time-control of the polymerization process and minimal heat production, in comparison with other techniques [68]. Photo-polymerization can be induced by ultraviolet (100-400 nm), visible (400-700 nm) or infrared (780-20000 nm) radiation. Light quanta are absorbed by molecules via electronic excitation [66]. During photo-polymerization process, photo-initiators are generally used having high absorption capacities at specific wavelengths of light thus enabling them to produce radically initiated species [69].

The preparation of a clay mineral-polymer composite with light for initiation of polymerization requires suitable monomers and a suitable photoinitiating system. In the research PNI-PAM/clay nanocomposite hydrogels were synthesized using aqueous dispersion of organoclay (O-MMT) particles, modified by distearyldimethyl ammonium chloride (Nanofil 8, Süd Chemie, Germany) in varied concentrations (0, 0.25, 0.5, 0.75, 1 wt% regarding the monomer content). Aqueous dispersions of different concentration of O-MMT were kept under constant stirring for 2 hours at room temperature after the addition of 1% NIPAM and 1 wt% (regarding the monomer content) BIS. After this period, 1 wt% (regarding the monomer content) Irgacure 2959 photoinitiator was added and the dispersion was kept under the same

conditions for additional 1 hour. Prepared dispersions were poured in glass Petri dishes, bubbled with nitrogen for 5 minutes and covered. Petri dishes were placed on the sample holder in the middle of a UV chamber (Luzchem). Polymerization was carried out in UV chamber using 6 UVA lamps (centred at 350 nm) placed on top of the chamber with the distance to the sample 15 cm. Time of polymerization was 2 hours. After polymerization the hydrogels were washed with deionised water for 4 days (daily exchange of water). After washing, the hydrogels were dried at 40°C until a constant mass was reached. Preparation scheme is presented in Figure 2.

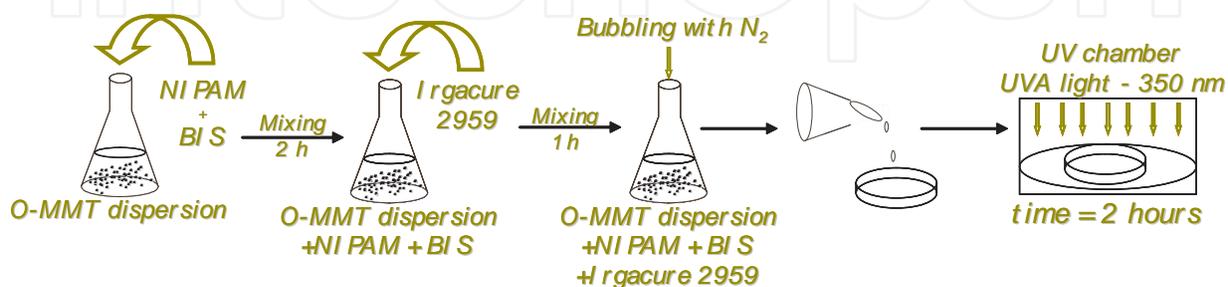


Figure 2. Nanocomposite hydrogel preparation process.

3.2. Clay/polymer nanocomposite hydrogel structure

Wide angle (WAXS) or small angle X-ray scattering (SAXS) are generally used methods for characterization of nanocomposite structure. These techniques enable determination of the spaces between structural layers of the silicate utilizing Bragg's law: $\sin\theta = n\lambda/2d$, where λ corresponds to the wave length of the X-ray radiation used in the diffraction experiment, d the spacing between diffraction lattice planes and θ is the measured diffraction angle [70]. By monitoring the position, shape and intensity of the basal reflection from the distributed silicate layers, the nanocomposite structure may be identified [71].

Depending on the nature of the components used (clay mineral, organic cation and polymer matrix) and the method of preparation, three main types of composites may be obtained when a clay mineral is combined with polymer. Then the polymer is unable to be intercalated, a phase-separated composite is obtained, whose property stay in the same range as those of traditional micro composites. Beyond this classical family composite, two further types of nanocomposites can be obtained. An intercalated structure in which a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers results in well-ordered multilayers morphology built up of alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained [70] Intercalated structures can be identified using SAXS or WAXS analyses [46,72].

To analyse the effect of monomer, crosslinker and photoinitiator content on composite structure formation we have prepared dispersion of MMT particles, monomer, crosslinker and photoinitiator to study the influence of reagents on MMT particles intercalation by measur-

ing distances between silicate galleries of clay particles using small angle X-ray scattering (SAXS). Figure 3 shows two x-ray diffraction curves of O-MMT particles which were dispersed in monomer, crosslinker and photoinitiator water dispersion.

On the diffraction curve of O-MMT particles dispersed in water, the characteristic maximum for O-MMT particles ($q = 2,8 \text{ nm}^{-1}$) is observed. According to the Bragg's law it corresponds to the distance between silicate layers $d_{001} = 2.03 \text{ nm}$. By the addition of monomer, crosslinker and photoinitiator into the O-MMT dispersion, the characteristic discrete maximum on the diffraction curve is shifted to a lower angle value ($q = 1,65 \text{ nm}^{-1}$) which corresponds to the distance between silicate layers $d_{001} = 3,81 \text{ nm}$. According to the pronounced change in silicate layers distances, we are concluding that monomer molecules have intercalated between silicate layers.

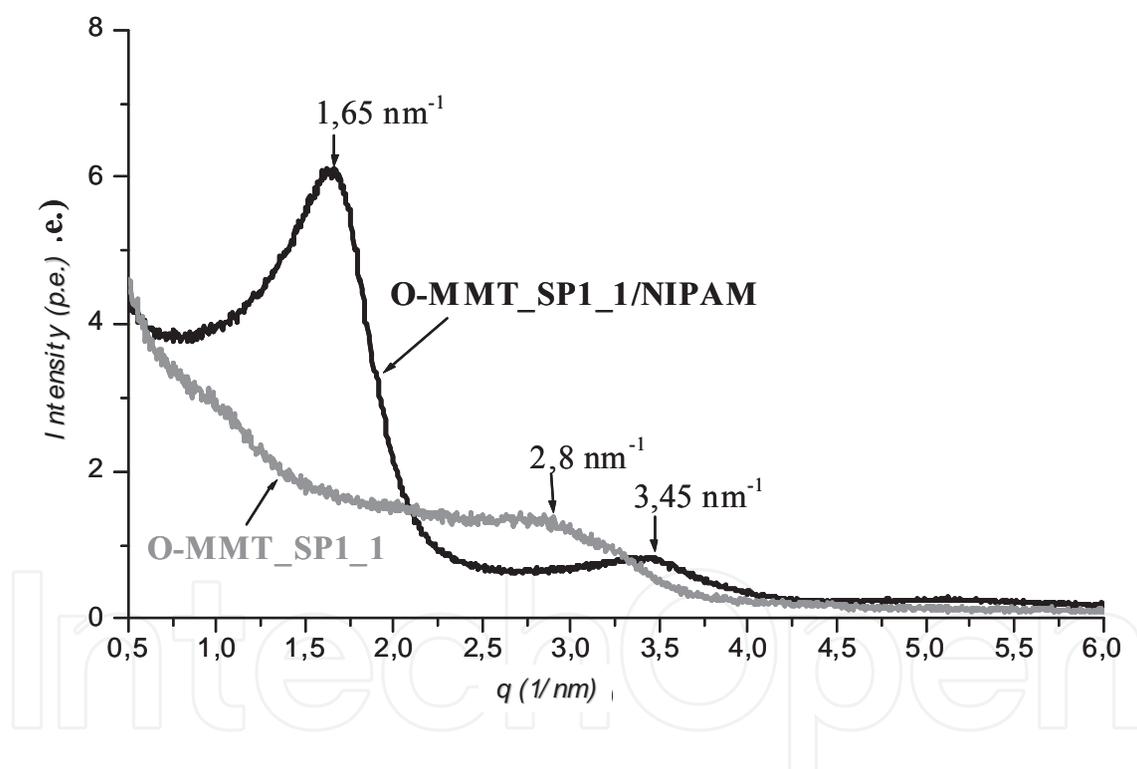


Figure 3. SAXS-pattern of O-MMT particles and O-MMT particles dispersed in monomer, crosslinker and photoinitiator solution.

Thereby silicate layers are pushed apart which increases the distance between them, however the repetitive silicate multi layer structure is still preserved, allowing the interlayer spacing to be determined. By addition of monomer, crosslinker and photoinitiator into O-MMT aqueous dispersion, we obtained O-MMT dispersion with intercalated structure of O-MMT particles as shown in Figure 4.

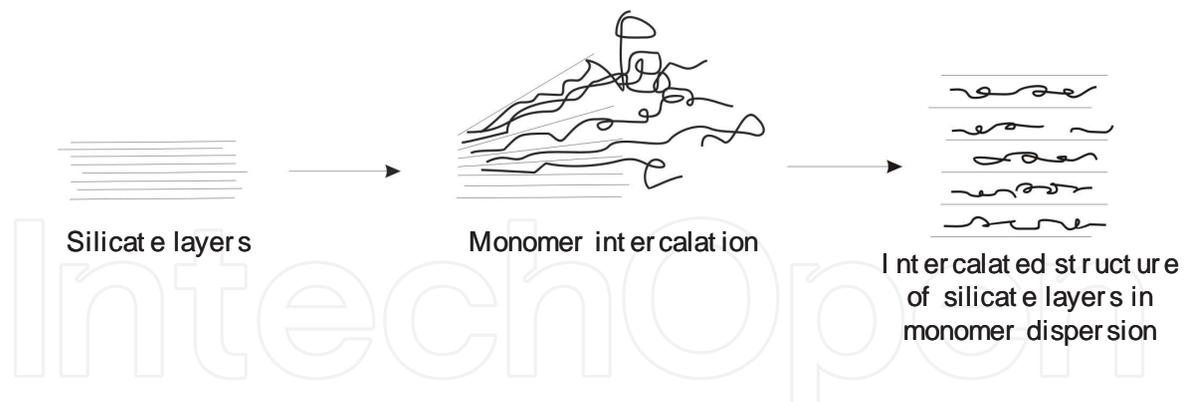


Figure 4. Intercalation of monomer, crosslinker and photoinitiator molecules between clay minerals silicate layers.

Since nanocomposite material is formed when the complete exfoliation of silicate platelets is possible, in-situ polymerized hydrogels were also analyzed using SAXS. Figure 5 presents x-ray spectra of composite hydrogels with different concentrations of O-MMT particles (0,25; 0,5; 0,75; 1 wt%).

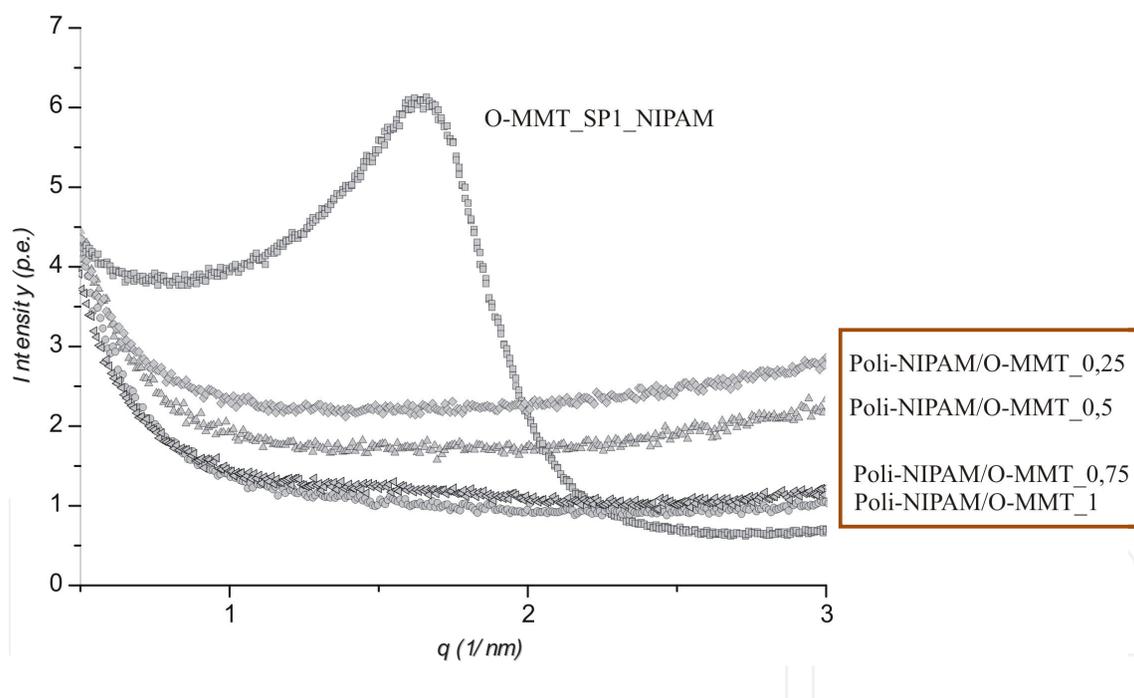


Figure 5. SAXS pattern of O-MMT particles dispersed in monomer, crosslinker and photoinitiator solution (O-MMT_SP1_NIPAM) and nanocomposite hydrogels (Poli-NIPAM/O-MMT) with different clay content.

The discrete maximum at $q=1.65 \text{ nm}^{-1}$ characteristic for O-MMT particles dispersed in monomer solution, disappears on small angle scattering curves of nanocomposite hydrogels. This phenomenon indicates that monomer molecules between platelets galleries polymerize and crosslink due to UV irradiation. Polymer formation causes movement of clay platelets apart and thereby the exfoliated structure of polymerized O-MMT/NIPAM nanocomposite hydrogel is formed.

In contrast to the intercalated structure, the extensive layer separation associated with exfoliated structures disrupts the coherent layer stacking and results in a featureless diffraction pattern. Thus, for exfoliated structures no more diffraction peaks are observed in X-ray diffractograms either because of a much too large spacing between the layers, (i.e. exceeding 8 nm in the case of ordered exfoliated structure) or because the nanocomposites did not present ordering [70,71,73].

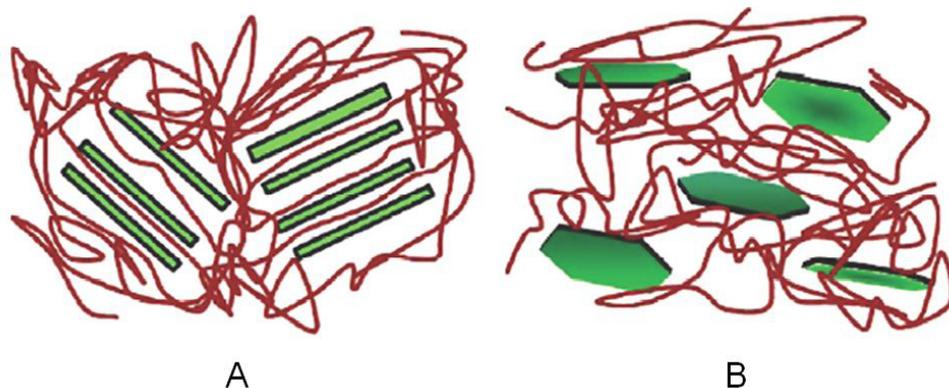


Figure 6. Scheme of intercalated and exfoliated nanocomposite structure [71].

3.3. Clay/polymer nanocomposite hydrogel swelling and gel fraction

The weight ratio of the dried hydrogels in rinsed and unrinsed conditions can be assumed as a measure of crosslinking degree or gel fraction. Therefore the gel fraction of sample can be calculated as follows [74]:

$$\text{Gel fraction (\%)} = \frac{W_f - W_c}{W_i - W_c} \times 100$$

Where W_f and W_i are the weight of the dried hydrogel after and before rinsing, respectively and W_c is the weight of organoclay incorporated into the sample.

To perform gel fraction measurement, pre-weighed hydrogel sample was dried under vacuum at room temperature until no change in mass was observed.

A typical dependency of the gel fraction on the clay concentration in hydrogels is given in Figure 7.

Gel fraction of samples is increased by increasing the amount of clay. The relationship is almost linear. The gel fraction data reveal that presence of clay within the three dimensional networks of hydrogels causes an increase in crosslinking, thus creates more entangled structure. By adding O-MMT to the hydrogel, strong interactions are developed between functional groups of organoclay and polymer chains.

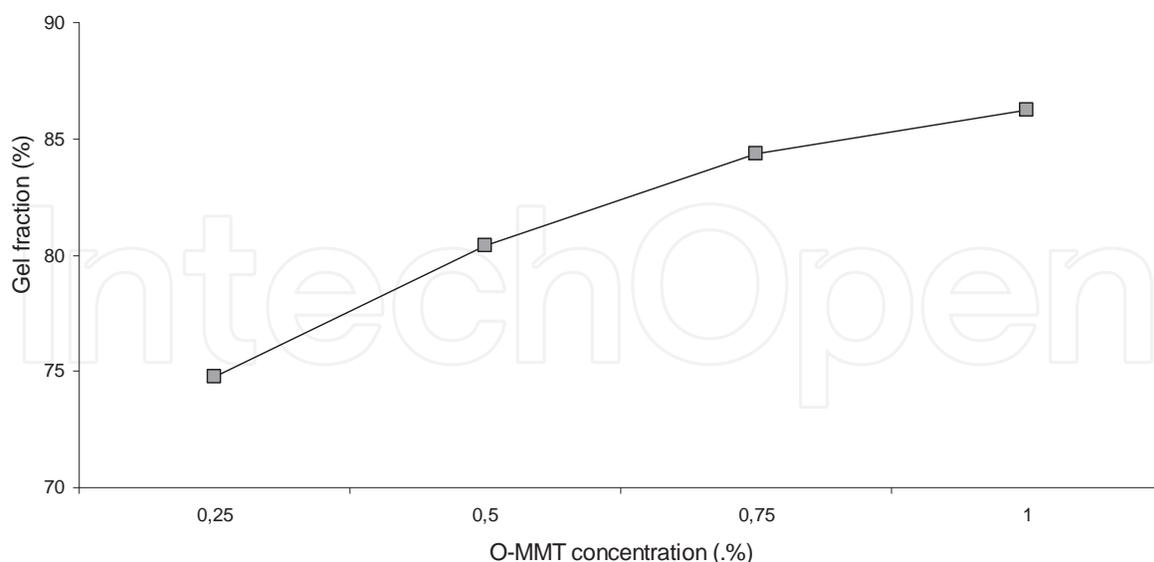


Figure 7. Gel fraction of nanocomposite hydrogels regarding the O-MMT clay concentration.

When pre-weighed samples of nanocomposite hydrogels are kept in water, the compact (dry) network structure of the polymer matrix relaxed and swells due to the diffusion of water molecules into the matrix until equilibrium is reached. At this stage, pressure inside the hydrogel matrix increases due to the presence of large amount of water molecules. Cross-linked structure prevents the dissolution of hydrogels [43].

For determination of an equilibrium swelling degree (EDS), we used pre-weighed hydrogel samples and immersed them into deionised water. Samples were removed from water every hour, wiped with filter paper in order to remove surface water, weighted and placed back into the water for further swelling. The equilibrium was reached when no mass difference was determined. EDS was calculated using the equation [46]:

$$EDS(\%) = \frac{W_s - W_d}{W_d} \cdot 100 \quad (1)$$

where W_s and W_d are the masses of the gel in swollen and dried states, respectively.

When hydrogel is exposed to water, water molecules diffuse into hydrogel structure and consequently hydrogel swells. Hydrogel ability to swell or uptake water is one of its key characteristics.

Figure 8 demonstrates the equilibrium degree of swelling (EDS) of NIPAM hydrogel and NIPAM/clay nanocomposite hydrogels as a function of the amount of clay. Decreasing trend of equilibrium swelling degree by increasing the quantity of organoclay is observed.

By comparing the equilibrium swelling degree and gel fraction values (Figure 7) a relationship between these properties is observed, i.e. more gel fraction leads to less swelling. Dens-

er hydrogel structure which is formed by increasing clay particles concentration affects the water uptake and decreases the swelling degree. Water uptake represents the migration of water molecules into preformed gaps between polymer chains [75]. Denser hydrogel structure diminish the accessibility of water molecules to hydrophilic parts of polymer molecules, therefore less water can penetrate into the hydrogel structure.

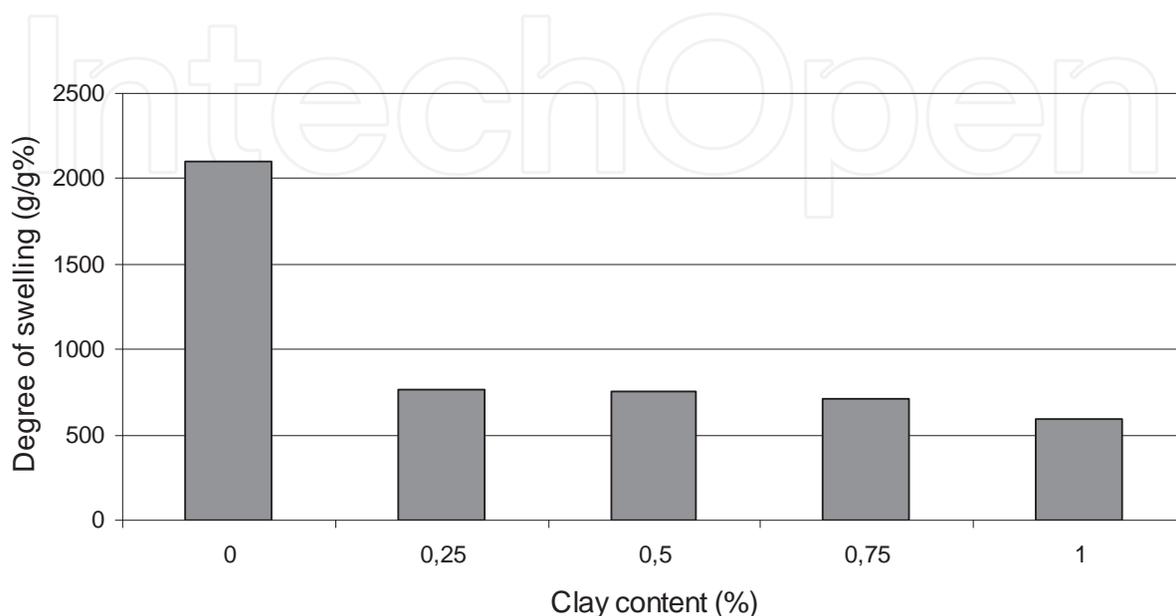
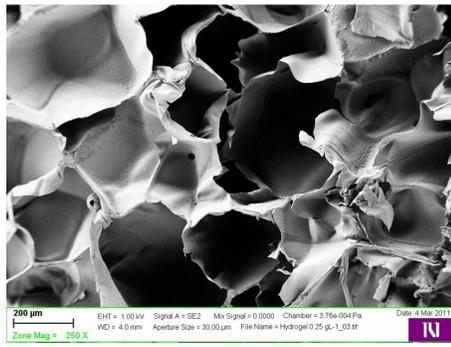


Figure 8. Degree of swelling for hydrogel and nanocomposite hydrogels with different clay content.

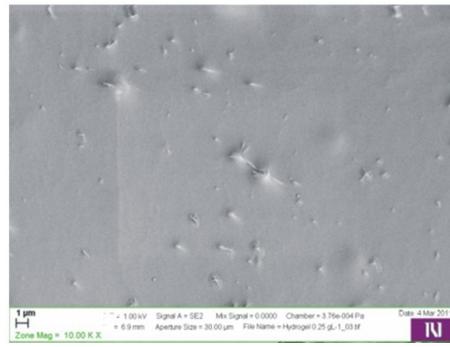
3.4. Clay/polymer nanocomposite hydrogel morphology

Figure 9 shows SEM micrographs of a cross-section and a pore surface of nanocomposite hydrogels with different clay content. Samples were lyophilized after the equilibrium swelling has been reached at room temperature in order to preserve natural nanocomposite hydrogel structure in swollen state. Nanocomposite hydrogel cross-section (Figure 9 A/I, B/I, C/I, D/I) shows very porous structure with several pores and wide pore size distribution. The pore structure has a sponge-like shape with spherical opens and interconnected cells. This porous microstructure is essential for a large active surface of hydrogel and assures the capillary effect of water uptake. Comparing the hydrogels pore structure regarding the clay content we observed a drastic change in pore size for nanocomposite hydrogel with 1 wt% O-MMT particles in the hydrogel matrix. At the concentration of 0.25 % O-MMT particles the pore size is approximately 200 μm , while the pore size for nanocomposite hydrogel with 1% O-MMT particles is 100 μm . This pore size reduction confirms that silicate platelets represent additional crosslinking points in nanocomposite hydrogel structure.

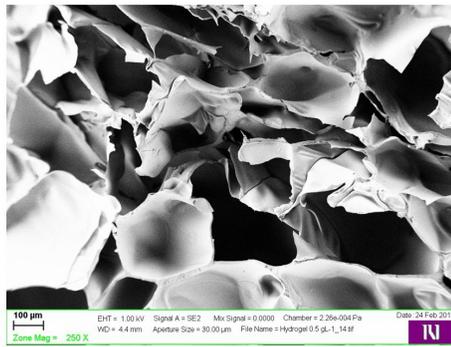
Figures 9 A/II, B/II; C/II and D/II show pore surfaces of nano-hydrogels. On the surface incorporated clay particles are observed.



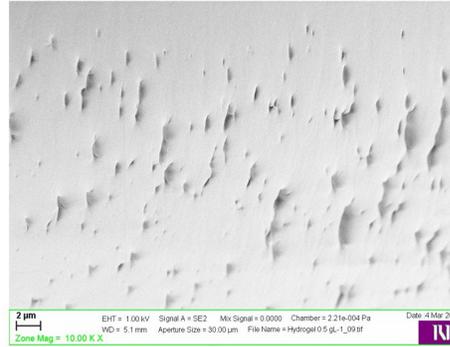
A/I



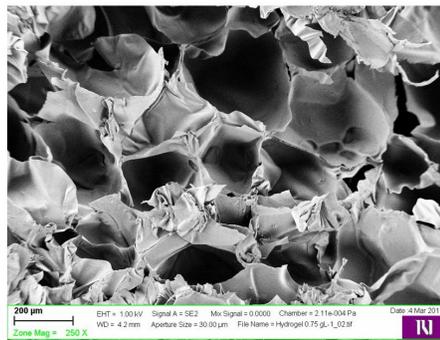
A/II



B/I



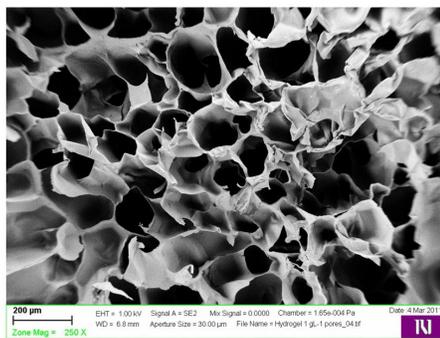
B/II



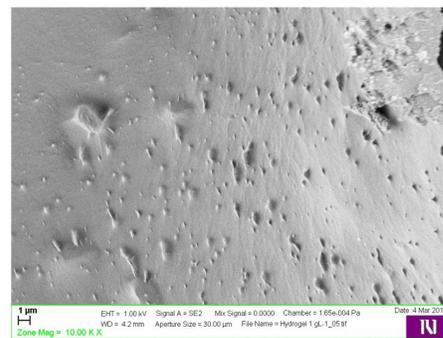
C/I



C/II



D/I



D/II

Figure 9. SEM of freeze-dried nanocomposite hydrogels with different clay content (A: hydrogel with 0.25% O-MMT; B: hydrogel with 0.5% O-MMT; C: hydrogel with 0.75% O-MMT; D: hydrogel with 1% O-MMT).

4. Adsorption properties of clay/polymer nanocomposite hydrogels

Adsorption studies are the key for evaluating the effectiveness of an adsorbent. Montmorillonite particles used for preparation of nanocomposite hydrogels are organically modified and therefore contain positively charged nitrogen atoms that attract opposite negatively charged anions with electrostatic attraction. Binding efficiency was studied with determination of adsorption degree. To study the effects of different experimental parameters, such as, pH, dye concentration, clay structure on the adsorption of anionic dye Acid Orange 33 onto clay/polymer nanocomposite hydrogel, UV spectroscopy was used. A Carry 50 spectrophotometer (Varian) was used for analyses. The dye concentration was determined at a wavelength corresponding to the maximum absorbance. The adsorption degree was calculated using following equation [43]:

$$\text{Adsorption degree (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

Where C_0 and C_e are the initial and equilibrium concentrations of Acid Orange 33 dye (mg/L), respectively.

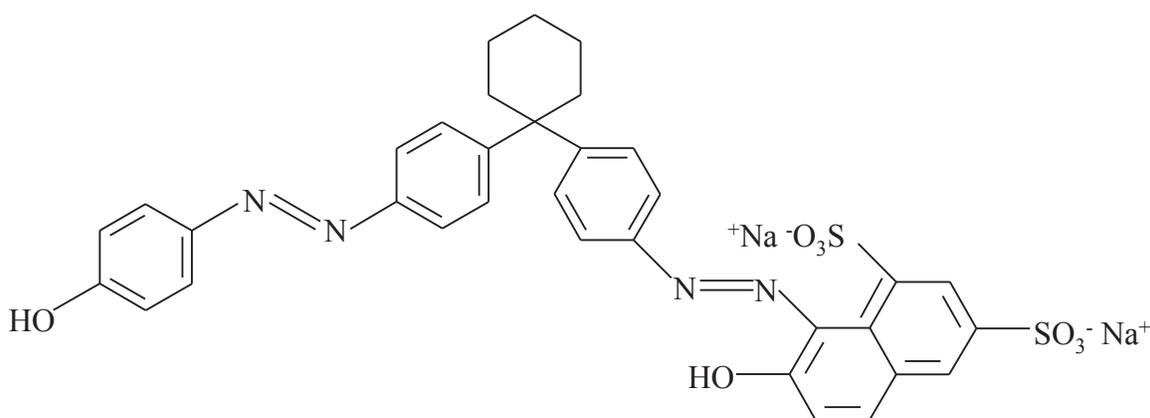


Figure 10. Chemical structure of Acid Orange 33.

Acid Orange 33 is an anionic dye used for dyeing wool, silk and PA, since it contains negatively charged SO_3^- groups in the structure (Figure 10).

4.1. Adsorption degree: pH dependence

pH of the solution is one of the main parameters that control the adsorption process. The effect of pH solution depends on the ions present in the reaction mixture and electrostatic interactions at the adsorption surface [43]. To determine the effect of different pH on Acid Orange 33 dye removal, the adsorption was carried out at different pH values of dye solution (pH= 3-9). pH was adjusted using acid/base buffer solutions. Figure 11 presents the effect of pH on the dye adsorption at an initial dye concentration of 100 mg/L.

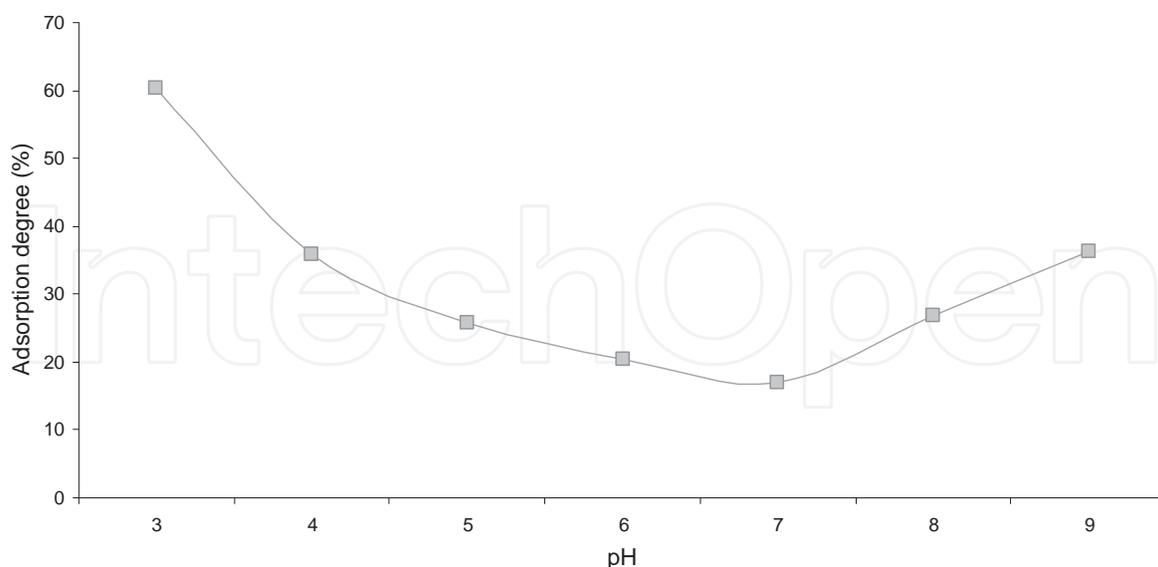


Figure 11. Adsorption degree vs. pH.

In Figure 11 the highest dye adsorption degree is observed at pH = 3 (around 60%). We assume that this high dye adsorption onto clay/polymer nanocomposite hydrogel at low pH values is due to the neutralization of the negative charge of $-\text{SO}_3^-$ anion, which influences the protonation and thereby increases the electrostatic attraction between the negatively charged $-\text{SO}_3^-$ anion and the positively charged adsorption site. The reason for high adsorption capacity at low pH is due to the strong electrostatic interaction between the cationic surfactant head groups of clay minerals incorporated in the hydrogel matrix and dye anions [4].

By increasing the pH to higher, neutral values (pH=4-7) we observe a decrease in adsorption degree. This is due to the decrease of positive charge on the clay surface and the number of negatively charged sites increases. The negatively charged surface sites on clay do not favour the adsorption of anionic dye due to the electrostatic repulsion [76].

In alkaline pH region (pH=8-9) we observe another slight increase in adsorption degree, which is lower regarding the adsorption at pH = 3. Barkaralingam et al. reported that in alkaline medium a competition between OH^- ions and dye anions will be expected [76], however a significant colour adsorption is still observed as the pH of dye solution increases from 7 to 9. He suggested that a second mechanism is operating at these conditions. The mechanism of colour removal at higher pH values can be explained by formation of covalent bonds between the external surface $-\text{OH}$ groups of Si and Al atoms of adsorbent and negatively charged dye molecules [10].

The maximum adsorption degree of Acid Orange 33 is at pH =3, which was therefore selected for all further adsorption experiments.

4.2. Adsorption degree - adsorption time dependence

The effect of adsorption time on the adsorption capacities of Acid Orange 33 is shown in Figure 12. The adsorption capacity increased rapidly within the first 60 minutes, after that it increased slowly until the adsorption equilibrium was reached. Under experimental conditions (1 wt% O-MMT, 0,1g/L Acid Orange 33 and pH3), the equilibrium time for the adsorption of Acid Orange 33 onto clay/polymer nanocomposite is 360 minutes. The rapid adsorption observed during the first 60 minutes is probably due to the abundant availability of active sites on the clay surface, and with the gradual occupancy of these sites, the adsorption becomes less efficient [77].

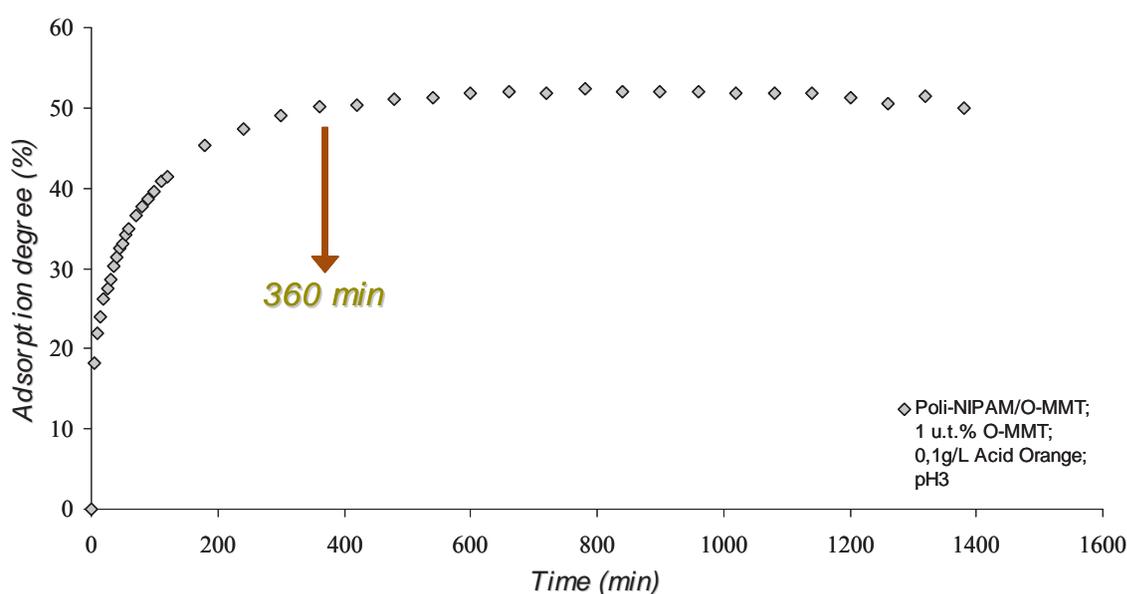


Figure 12. Degree of swelling vs. time.

4.3. Adsorption degree - initial dye concentration dependence

Generally, the removal of dye is dependent on the initial concentration of the dye in the solution. Results shown in Figure 13 indicate that the equilibrium dye uptake by nanocomposite hydrogel increases with increasing initial dye concentration. This is because at higher initial dye concentration, the availability of the number of dye molecules is higher, which can easily penetrate through hydrogel matrix. However, the removal efficiency is increasing only slightly after the initial dye concentration 0.05 g/L. This can be due to the saturation of hydrogel sites [43] or due to the fact that the formation of dye molecules agglomerates makes it almost impossible for them to diffuse deeper into the nanocomposite hydrogel [78].

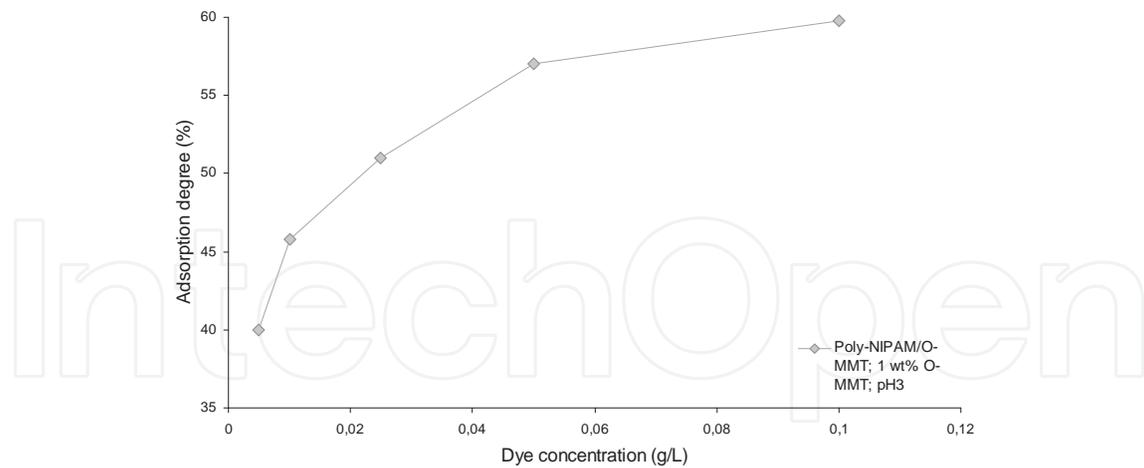


Figure 13. Adsorption degree vs. initial dye concentration.

4.4. Adsorption degree - O-MMT clay particles concentration dependence

The effect of the amount of active sites was studied by using hydrogels with different concentration (0.25 – 5%) of O-MMT particles incorporated in hydrogel matrix. The adsorption degree was measured in a solution containing 100 mg/L Acid Orange 33 dye at pH3. Figure 14 shows that the removal of the dye from the solution increases with an increase in the quantity of O-MMT particles incorporated into the hydrogel matrix. This indicates that the presence of higher quantity of O-MMT particles provides a larger number of active sites, which are positively charged and are capable to absorb more Acid Orange 33 dye molecules due to electrostatic forces. From the results we can conclude that the adsorption degree is significantly increasing from 30 to 59,9% when the concentration of nanoparticles increases (from 0.25 to 1% of O-MMT), but with additional increase of O-MMT particles in hydrogel matrix there is no change in the adsorption degree (the adsorption degree is 60,3% for the hydrogel containing 5% of O-MMT). We assume that at higher clay concentrations agglomerates are formed inside the hydrogel matrix, and therefore the expected additional active sites are not formed [78].

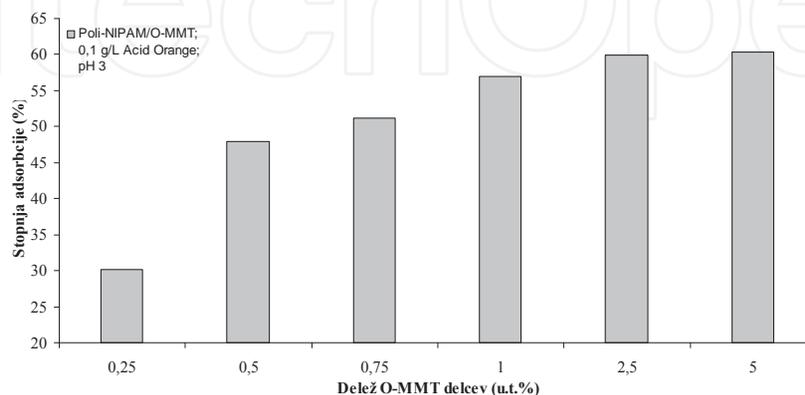


Figure 14. Adsorption degree vs. clay concentration.

5. Conclusions

Hydrogel nanocomposites have been prepared and their potential to be used as adsorbent materials for the removal of dyes which is a serious problem, especially in the textile industry was studied.

It was shown that incorporation of O-MMT particles into the hydrogel matrix induced adsorption capability for acid dye Acid Orange 33. The results obtained from adsorption study show that:

The adsorption capacity is maximal at the pH value 3 of the dye solution and is decreasing with increasing pH.

The equilibrium time for the adsorption of Acid orange 33 onto clay/polymer nanocomposite is 360 minutes.

Equilibrium dye uptake by nanocomposite hydrogel increases with increasing initial dye concentration.

As the content of O-MMT particles in hydrogel matrix increases, adsorption capacity is increasing. At O-MMT content higher than 1wt% the adsorption capacity remains unchanged.

Author details

Manja Kurecic* and Majda Sfiligoj Smole

*Address all correspondence to: manja.kurecic@uni-mb.si

University of Maribor, Faculty of Mechanical Engineering, Department for Textile Materials and Design, Slovenia

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