Physicochemically modified peat by thermal and oxidation processes as an active material for purification of wastewaters from certain hazardous pollutants

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Abstract
The physicochemical modification of peat through thermal and oxidation processes was carried out, in order to obtain new, inexpensive and active material for purification of different types of waters. During the modification, surface chemical compounds of Shilov type were formed. Batch adsorption properties and suitability of physicochemically modified peat (PCMP) for odor removal were tested in aqueous solutions of H2S and colloidal sulphur. Additionally, PCMP was tested in the removal of As(V) which is hazardous ingredient in contaminated waters. Possible mechanisms of pollutants binding include interactions, which lead to formation of adducts and clathrates. All these processes are elucidated in detail. The results showed that the obtained material can be used for the removal of sulphide, colloidal sulphur and As(V) from different types of waters.

Keywords: peat, physicochemical modification, surface groups, arsenic, hydrogen sulphide, adsorption-sorption.

EXPERIMENTAL

Natural peat and physicochemically modified peat

Raw peat was obtained from Dallas Company, Serbia, and used as received. Physicochemical properties and elemental composition of raw peat which was used in the study are shown in Table 1.

XRD technique was used for further examination of the mineralogy of the peat samples by using Siemens D500 diffractometer. Results of analysis indicate silicate and aluminosilicate crystalline structures, mostly quartz, cristobalite and kaolinite.

Peat was washed with distilled water, dried at room temperature, and then triturated in a mortar with...
pestle, and finally sieved (8 mesh). A suspension of the peat (50 g in 300 cm$^3$ of 1 M CaCl$_2$ solution) was stirred on a magnetic stirrer, and subsequently heated at 95 °C for 1 h. After cooling, the suspension was filtered on a Buchner funnel under vacuum and then the resulting Ca$^{2+}$-peat dried in an oven at 105 °C. The entire mass was transferred to a porcelain crucible and thermally modified by heating to 230 °C at a rate of 6 °C/min and thermal treatment was continued for 3 h. After cooling, the material was suspended in 0.1 M HCl and stirred in a magnetic stirrer, and then filtered on a Buchner funnel under vacuum. The process was repeated twice, and then the material was washed with plenty of hot deionized water. The resulting material was dried and labeled as physico-chemically modified peat (PCMP).

### Table 1. Physicochemical characteristics of peat

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.9</td>
</tr>
<tr>
<td>Content of solids</td>
<td>59.2%</td>
</tr>
<tr>
<td>Total inorganic solids</td>
<td>6.5%</td>
</tr>
<tr>
<td>Total organic matter</td>
<td>52.7%</td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>0.7%</td>
</tr>
<tr>
<td>Ratio C/N</td>
<td>26.3</td>
</tr>
<tr>
<td>Moisture</td>
<td>40.8%</td>
</tr>
</tbody>
</table>

The chemical structure and functional groups of the raw and modified peat samples were analyzed by Fourier transform infrared spectroscopy (FTIR, Bruker Tensor). Morphology was recorded by using scanning electron microscopy JEOL JSM-6610LV.

**Conductometric titration**

PCMP was suspended in a 1% solution of NaHCO$_3$ and after stirring filtered and washed with deionized water and then used for further examination by conductometric titration.

The total concentration of acidic groups on the surface of PCMP was determined by conductometric titration of suspension which contained 0.2 g PCMP in 50 cm$^3$ of deionized water. In order to estimate concentration of strong and weak acid surface groups, one sample of the suspension was titrated with a 0.05 M NaOH solution, and the other with 0.025 M HCl. All titration experiments were carried out in duplicate or triplicate and final results presented were given as mean value.

**Removal of sulphur from waters containing H$_2$S (HS$^-$ and S$^2$), colloidal sulphur and corresponding sulphur anions**

Synthetic water containing 15 mg/l of sulphide (S$^{2-}$) was prepared by dissolving an appropriate amount of Na$_2$S·9H$_2$O in deionised water which had previously been deoxigenated through purging with N$_2$. Finally, pH was adjusted to 12 and 250 ml and synthetic water was contacted with 1 g of PCMP in hermetically closed vessel. Agitation was enabled by using magnetic stirrer. After contact time of 25 min suspension was filtered and concentration of sulphide was determined by WTW inoLab pH 730 using Ag/S ion-selective electrode. Synthetic water containing colloidal sulphur was prepared according to the following chemical reaction:

$$\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{S} + \text{SO}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$ (1)

White-yellow sol was used for further experiments of colloidal sulphur removal onto PCMP in batch system.

**Arsenic(V) removal from synthetic water**

The amount of 1 g PCMP was suspended in synthetic water which contained calculated amount of Na$_2$HAsO$_4$·7H$_2$O to obtain As(V) concentration of 150 μg/dm$^3$. Turbid suspension was obtained which then filtered after 25 min of contact time and continuous agitation on magnetic stirrer. The concentration of As in filtrate was determined by hydride generation atomic absorption spectrometry (HG-AAS) using Perkin–Elmer atomic absorption spectrophotometer.

**RESULTS AND DISCUSSION**

**Physicochemical properties of peat and surface chemical compounds of Shilov type**

By partial destruction of surface structure of natural peat using thermal treatment and layering of the obtained products, very active surface chemical compounds were obtained which readily interact with certain pollutants in urban wastewaters and synthetic waters containing sulphide, colloidal sulphur, corresponding sulphur anions and arsenic(V). During a thermal modification, the activation of cellulose and lignin, as well as a partial polymerization of humic and fulvic acids occurred [9]. According to the hypothesis of Shafizadeh and Bradbury positions 1 and 4 on the glucose units of cellulose are most susceptible to oxidation, but other positions may also react with oxygen [10]. In the first step the radicals were formed, which during further reaction resulted in forming of peroxides or beta cleavage, causing a dehydration or depolymerization of cellulose. According to literature, both reactions are very fast compared to the reaction of formation of radicals. In the temperature range 160 to 220 °C depolymerization is much more pronounced than the dehydration of the cellulose, which is accompanied by the formation of surface oxygen groups [10]. Pyranose rings at the surface may form peroxides, whereby two stages can be distinguished. The first involves detachment of hydrogen atoms under the action of oxygen and the formation of perhydroxyl (HOO$^\cdot$) or hydroxyl...
(HO•) radicals. The second stage is determined by the decomposition of peroxyde. Hence, for the formation of surface active groups and surface chemical compounds of Shilov type, crucial role has been ascribed to adsorption of oxygen [11]. Each squared centimeter can adsorb around $10^{15}$ oxygen atoms forming ketones and heterocyclic compounds, as well as –OH, –COOH and hydroperoxyde functional groups. Shilov developed concepts on the origin of surface chemical compounds capable of redox reactions and ion-exchange with the ions of electrolytes. Hence, the adsorption layer of oxygen formed negative charge and enabled oxidation of solid phase and formation of mobile cations. For this reason, further adsorption of oxygen was continued and reduction occurred onto small clusters. Such formed area at which redox process is occurring are called redoxites [11]. These surface chemical changes are accompanied by the release of energy. Surface chemical compounds – oxides can be represented by Shilov theory as shown by Eq. (2):

$$\begin{align*}
\text{C-O} + 0.5\text{O}_2 & \rightarrow \text{C=O} + 0.5\text{O}_2^+ \\
\text{C=O}^+ + \text{H}_2\text{O} & \rightarrow \text{C=O} + \text{H}_2\text{O}
\end{align*}$$

In the reaction with water, Shilov oxides form acid or base hydrates. According to Shilov, adsorption of acids is neutralization reaction; Eq. (3) is as follows:

$$\text{C-OH} + \text{H}^+ + \text{An}^- \rightarrow \text{CAn} + \text{H}_2\text{O}$$

This reaction can be conditionally designated as hydrolytic adsorption and essentially it is surface exchange reaction. In addition to the neutralization and exchange reactions, surface compounds participate in redox reactions. An important process of organic substrates oxidation in accordance with the theory of Shilov can be illustrated by the reaction – Eq. (4):

$$\begin{align*}
\text{C} + 0.5\text{O}_2 & \rightarrow \text{C=O} + 0.5\text{O}_2 \\
\text{C}=\text{O} + 0.5\text{O}_2 & \rightarrow 2\text{CO}_2
\end{align*}$$

This surface compounds were formed at the temperature of thermal treatment of peat due to energy of chemical bond formation as well as external energy are not sufficient for the detachment of surface atoms and formation of CO₂. Therefore, the last reaction step (Eq. (4)) did not take place significantly.

**FTIR analysis**

FTIR analysis revealed main functional groups and surface compounds of Shilov type in composition of peat and PCMP. In both spectra shown in Fig. 1 the broad peak at 3412 cm⁻¹ can be attributed to the O–H and/or N–H stretching vibrations. This absorption zone revealed a lowering in relative intensity of –OH stretch content of the PCMP, due to the removal of adsorbed water in Ca-peat during thermal treatment. The low-intensity peaks at 3698, 3622, 531 and 471 cm⁻¹ marked with an asterisk are attributed to presence of silica, silicates and clay minerals. The peaks appearing at 2975, 2921 and 2851 cm⁻¹ are due to C–H stretching vibrations of –CH, –CH₂ and –CH₃ groups which are usually considered to indicate the presence of fatty acids and wax in peat samples [12]. The peaks at 1608–1635 cm⁻¹ and 1711 cm⁻¹ were attributed to asymmetric carboxyl stretching of carboxylate and carboxylic acid, respectively [12,13]. The signal of carboxyl stretching vibration of carboxylic acids is barely noticeable in the spectra of Ca²⁺-peat and clearly evident as a rather weak shoulder in the case of PCMP. The C=O bands at 1608–1635 cm⁻¹ were clearly observed and shifted slightly toward lower values of wavenumbers for PCMP. The appearance of band corresponding to carboxylic acid could be explained by protonation of free carboxylic groups. The intensity of carboxylate peaks for samples of Ca-peat and PCMP are almost equal indicating that no significant decomposition of carboxylic groups into gaseous products (decarboxylation) occurred. The intense peak at 1041, 1084 and 1268 cm⁻¹ are due to C–O and C–N stretching vibrations. Aromatic ring C=C stretching appears at 1511 cm⁻¹.

The shoulder-type peak around 1041 cm⁻¹ and the broad hydroxyl band centered at 3412 cm⁻¹ are ascribed to polysaccharide [13]. Similarly, the carbohydrate peak lies close to the silicate absorption band at 1084 cm⁻¹ (all of samples contained small fraction of ash up to 7%). The bands assigned to lignin are observed at 1511, 1458, 1391, 1268 and 838 cm⁻¹.

**SEM characterization**

SEM images are illustrated in Fig. 2. The untreated peat sample showed typical characteristics of natural peat, with aggregates of platelike or irregular shaped particles in random order (Fig. 2a). The modified peat...
samples contained clearly visible aggregates with a smooth surface (Fig. 2b).

Conductometric titrations

Conductometric titration of PCMP suspensions with acid is shown in Fig. 3. An equivalence point ($V_{k1}$) was achieved after the addition of 2.26 cm$^3$ of 0.025 M HCl.

During the titration before $V_{k1}$, the following protolytic reaction on the surface occurred:

$$\text{Surf}_1^-\text{Na}^+ + H^+ \rightarrow \text{Surf}_1^-\text{H}^- + \text{Na}^+ \quad (5)$$

Different solid surface centers were assigned through text as $\text{Surf}_n$ with appropriate subscript number ($n$). The protons were bound to the surface, while an increase in conductivity was derived from the increase in the concentration of $\text{Na}^+$ and $\text{Cl}^-$. After the $V_{k1}$ point, protons added to a solution were free and directly contributed to the increase of conductivity. As the $H^+$ have a higher molar conductivity than $\text{Na}^+$, the second part of the curve has a greater slope. Surface groups denoted as $\text{Surf}_1^-\text{H}$ are the most acidic on the surface of PCMP, because during the preparation of materials they were neutralized by a weak base, i.e., a solution of $\text{NaHCO}_3$. The concentration of surface groups $\text{Surf}_1^-\text{H}$ is 0.282 mmol/g.
There are two equivalence points for the titration of PCMP suspensions with 0.05 M NaOH (Fig. 4). This indicates that on the surface there are two types of acid groups, of which one has a lower, and the other more pronounced acidic characteristics.

The reactions can be represented by the following equations:

\[ \text{Surf}_2\text{H} + \text{Na}^+ + \text{OH}^- \rightarrow \text{Surf}_2\text{Na} + \text{H}_2\text{O} \]  
\[ \text{Surf}_3\text{H} + \text{Na}^+ + \text{OH}^- \rightarrow \text{Surf}_3\text{Na} + \text{H}_2\text{O} \]

Before reaching the equivalence point \( V_{b1} \), protons bound to the surface \( \text{Surf}_2\text{C} \) centers were exchanged by \( \text{Na}^+ \), which then reacts with \( \text{OH}^- \) forming weakly dissociated \( \text{H}_2\text{O} \). From the point \( V_{b1} \) to \( V_{b2} \), NaOH reacts with the surface weaker acid centers \( \text{Surf}_3\text{H} \) (Eq. (7)), leading to the increase of the titration curve slope. After \( V_{b2} \), the concentration of free \( \text{OH}^- \) and the conductivity increase, which is observed as the second increase of a titration curve slope. The concentration of surface groups denoted as \( \text{Surf}_2\text{H} \) is 0.362 mmol/g, while concentration of the groups \( \text{Surf}_3\text{H} \) was estimated to be 0.420 mmol/g. Therefore, on the surface there are at least three types of acidic surface groups, which acidic strength can be put in the following order: \( \text{Surf}_1\text{H} > \text{Surf}_2\text{H} > \text{Surf}_3\text{H} \). Surface groups with the most prominent acidic character (\( \text{Surf}_1\text{H} \)) are most likely carboxylic groups, and their contribution on the surface is 26.53% of the total number of acid groups.

**Removal of \( \text{H}_2\text{S} \) and colloidal sulphur from synthetic water using PCMP**

The results obtained by analysis of synthetic water containing \( \text{S}^{2-} \) before and after treatment with PCMP are shown in Fig. 5.

Based on the results of sulfide ions removal from synthetic water, it can be established that the peat very effectively removed the sulfide ions from the starting concentrations of 7.787 to 2.595 mg/dm\(^3\). PCMP possesses developed surface area and can manifests adsorption and ion exchange properties which are responsible for its good adsorption characteristics. Additionally, chemisorption of sulfide ions through establishing chemical bonds of sulfur with activated macromolecules on the surface of the peat is another pos-

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**Fig. 4. Conductometric titration of a suspension containing 4 g/dm\(^3\) PCMP with 0.05 M NaOH at 20 °C.**

**Fig. 5. Physicochemical parameters of synthetic water containing \( \text{S}^{2-} \) before and after the treatment with PCMP.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthetic water volume (cm(^3))</th>
<th>Contact time (min)</th>
<th>Concentration ( \text{S}^{2-} ) (mg/l)</th>
<th>Electrical conductivity (( \mu \text{S cm}^{-1} ))</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>250</td>
<td>-</td>
<td>7.787</td>
<td>1552</td>
<td>9.87</td>
<td>0.4</td>
</tr>
<tr>
<td>I</td>
<td>250</td>
<td>25</td>
<td>2.595</td>
<td>1019</td>
<td>8.85</td>
<td>1.3</td>
</tr>
</tbody>
</table>

O – synthetic water containing \( \text{S}^{2-} \)
I – synthetic water after treatment with PCMP
sible mechanism of sulfide retention. Since the starting sample had a high pH value (9.87) and very low turbidity (NTU 0.4), it is obvious that changing the pH value in contact with the peat is related to reduction of sulfide concentration to 2.595 mg/dm³. Increased turbidity of 1.3 NTU could be explained by releasing of fulvic and humic acid. The results of colloidal sulphur removal are shown in the Fig. 6.

The chemical reaction of colloidal sulfur formation is given by Eq. (2) from which the following ions that participate in the forming of colloids can be noticed: Na⁺; S₂O₃²⁻; H⁺; SO₄²⁻. In excess of Na₂S₂O₃, potential determining ions are S₂O₃²⁻, while Na⁺ are counterions of colloidal particle. The core is made of the elemental sulfur, and the structure of the colloidal micelle is as follows:

\[
\{m[SₙS₂O₃²⁻ 2(n-x)Na⁺]\}2xNa⁺ \tag{8}
\]

In the case of H₂SO₄ excess, potential determining ions are SO₄²⁻, and counterions are H⁺. Hence, the suggested structure of colloidal micelle is:

\[
\{m[SₙSO₄²⁻ 2(n-x)H⁺]\}2xH⁺ \tag{9}
\]

Under the condition that the obtaining of colloid carries out without excess of any reactant, SO₄²⁻ and Na⁺ participate in the formation of micelles:

\[
\{m[SₙSO₄²⁻ 2(n-x)Na⁺]\}2xNa⁺ \tag{10}
\]

This is a very complex colloid chemistry of sulfur which was used for preparation the highly stable colloids. Having in mind colloidal behavior of sulphur, the most probable processes onto PCMP which lead to the removal of sulphide and colloidal sulphur are: ion-exchange processes, chemical reactions with surface groups, redox processes onto surface, interaction between charged surface and colloids leading to electrophoretic deposition, etc.

Based on the analysis of experimental results in Fig. 6., it is observed that the PCMP effectively removed colloidal sulphur and decreased turbidity from 168 to 0.7 NTU. Moreover, anionic forms of sulphur have been successfully removed from water leading to significant reduction of very high starting concentration of total sulphur (3040 mg/dm³). PCMP possesses very developed surface area and can manifest adsorption and ion exchange properties as well as the formation of chemical bonds between the sulfur and activated macromolecules at the surface of the peat. During the treatment, sulphur was only partially removed due to the short time of interactions. Based on the obtained results, PCMP has been proved to be an effective medium for the removal of sulfur and its anions from the water, and at the same time does not violate the natural physicochemical properties of water.

**Arsenic removal from synthetic water**

By chemical and thermal activation of peat adsorption and ion exchange properties were essentially improved, causing a decrease in the concentration of arsenic in synthetic water. This was confirmed by results shown in Fig. 7, where the great changes in the concentration of As in synthetic water before and after

![Fig. 6. Physicochemical parameters of synthetic water containing colloidal sulphur before and after the treatment with PCMP.](image-url)
treatment with PCMP were observed. Therefore, these results proved that purifying of synthetic water was achieved using PCMP, which resulted in a significant reduction of As concentration in synthetic water. The obtained solution after filtering has turbidity of 0.4 NTU.

Reduction of As(V) onto redoxite area of PCMP led to formation of colloidal arsenic which can be deposited onto surface and within the pores of active mass. The following structure of colloidal micelle can be proposed:

\[
\{m[As_4]nAsO_4^{3-}3(n-x)Na^+\}xNa^+ \quad (11)
\]

The dominant processes onto PCMP are as follows: reduction process onto redoxite areas, electrophoretic deposition onto negatively charged regions, occlusion of colloidal As in porous areas of PCMP with electrostatic electricity, partial ion-exchange, formation of As monolayer with surface carbon atoms.

Regardless of significant lowering of As concentration, below of MAC value of 10 µg/dm³, 1 ml of treated water still contains 3.5×10¹⁴ ions of As.

CONCLUSION

A new approach to the chemical properties of peat has been established by using the concept of chemical compounds of Shilov type, chemistry of solids and the interactions within polymer structures. The thermochemical modification led to the oxidation of the surface of peat. Consecutively, additional oxygen groups were formed on the surface by radical mechanism and formation of peroxo radicals. Surface groups were identified by FTIR analysis. On the surface PCMP there are at least three types of surface acidic groups and their concentration on the surface were estimated by conductometric titration.

Colloidal sulphur, corresponding sulphur anions and sulfide were successfully removed from synthetic waters by adsorption processes onto active surface centers; layering and deposition of adducts onto pore walls, closed vacancies, cages, tunnels and canals of branched and degraded polymers of modified peat; formation of inclusion compounds – clathrates; van der Waals interactions; ion-exchange, etc. Formation of colloids was originally explained in detail through specific chemical reactions and appropriate structures of colloidal micelle.

Moreover, arsenic (V) as extremely hazardous pollutant in contaminated water was removed from synthetic water from concentration of 150 to 4.3 μg/dm³. Based on the obtained results it can be concluded that the PCMP is an effective material for the removal of ionic and colloidal pollutants from different types of water. Additionally, there is a reasonable possibility that this material can be used as filler in reactors and columns for wastewater treatment leading to development of new alternative technology.

Acknowledgement

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REFERENCES


IZVOD

TRESET FIZIČKO–HEMIJSKI MODIFIKOVAN TERMALNIM I OKSIDACIONIM PROCESIMA KAO AKTIVNI MATERIJAL ZA PREČIŠĆAVANJE OTPADNIH VODA OD ODREĐENIH OPASNIH ZAGAĐUJUĆIH SUPSTANCI

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(Naučni rad)

Fizičko–hemijska modifikacija treseta putem termalnih i oksidativnih procesa je izvršena u cilju dobijanja novog, jeftinog i aktivnog materijala za prečišćavanje različitih vrsta voda. Tokom modifikacije formirana su hemijska površinska jedinjenja Šilov (Šilov) tipa. Serija adsorpcionalnih svojstava i podobnost fizičko–hemijski modifikovanog treseta (PCMP) za uklanjanje mirisa je testirana u vodenim rastvorima H2S i koloidnog sumpora. Pored toga, PCMP je testiran u uklanjanju As (V) koji je opasan sastojak u zagađenim vodama. Mogući mehanizmi vezivanja zagađivača uključuju interakcije koje dovode do formiranja adukata i klateata. Svi ovi procesi su razjašnjeni detaljno. Rezultati su pokazali da dobijeni materijal može da se koristi za uklanjanje sulfida, koloidnog sumpora i As (V) iz različitih tipova voda.

Ključne reči: Treset • Fizičko–hemijska modifikacija • Površinske grupe • Arsen • Vodonik-sulfid • Adsorpcija-sorpcija