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Morpho-structural, adsorption and electrochemical characteristics of serpentinite

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ABSTRACT

Pollution control and water purification are the main concerns associated with hazardous component eliminations from wastewaters which have inspired the research, among the others, on various clay minerals as useful adsorbents. The aim of this study was to examine morphological, structural, adsorption, and electrochemical characteristics of serpentinite in order to check its potential for removal of cadmium and textile dyes from synthetic waters. SEM technique has provided a detailed insight into the surface morphology of serpentinite indicating irregularly shaped particles and lamellar aggregates which are characteristic of lizardite mineral. Crystal phases detected in composition of serpentinite by using XRD technique are lizardite and tiny amount of periclase. Serpentinite adsorption characteristics were investigated towards Cd^{2+} and anionic textile dyes (Procion red MX-5B, Procion orange and Ramazol black) in aqueous solutions. The main goal of the study was the reliable removal of hazardous Cd^{2+} at low initial concentrations (up to 200 $\mu g/dm^3$). Textile dyes were taken as the models of anionic organic pollutants in water. All the adsorption experiments were carried out in batch conditions by varying initial parameters such as concentration of pollutant, contact time, mass of adsorbent and pH. Based on the obtained results, serpentinite has proven to be efficient adsorbent with removal efficiency over 98% for the selected pollutants. Native serpentinite was further modified in order to obtain forsterite. Electrochemical characteristics of serpentinite and forsterite were examined by using cyclic voltammetry of solution of 0.1 M H_2SO_4 as acidic supporting electrolyte and $K_4[Fe(CN)_6]$ which was chosen as a redox model compound. Due to its specific structure, surface groups, morphology, and non-stoichiometric composition, serpentinite and forsterite exhibited prominent electrocatalytic activity.

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1. Introduction

Serpentinite is a widespread rock often occurring as a modified product of olivine and other magnesium-rich silicates. It has been found among metamorphic and igneous rocks and consists predominantly of one or more serpentine group minerals: antigorite, chrysotile, and lizardite, which chemical formula is $Mg_3Si_2O_5(OH)_4$ [32,15]. Basically, these phyllosilicates have the same crystal structure and chemical composition but they differ in the curvature of the lattice planes. Consequently, antigorite and lizardite are dense or fine-grained while crysotile is fibrous [14]. They all belong to the group of clay minerals [24].

Crystal structure of serpentinite is basically built from layers of silicate tetrahedrons connected to a brucite-like layers formed from octahedrons of $[MgO_2(OH)_4]^{6-}$. These composite layers can be bent in wave-forms or shaped into fibers which are mutually linked by weak hydrogen bonds [16,15]. Because of the numerous bonds these composite layers are held rather tightly together and thus they are not expandable. Serpentinite commonly contains Mg and Si with minor amounts of Fe, Ni, Al, Ca, Cr, and Ni [32]. Fe and Ni can, to some extent, replace Mg, while Al can to a lesser extent replace Si or Mg. Acid–base characteristics of serpentinite in water can be ascribed to the acidic silicate layers and basic brucite-like layers, which cause them to manifest its buffering properties in acidic and alkaline solutions. Serpentinite has a significant amount of bound water, hence it contains abundant —OH groups which are responsible for pH dependent surface charge and potentially good adsorption characteristics, which has not been thoroughly examined so far. Serpentinites are mainly used in industry as railway

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ballasts, building materials and thermal or electrical insulations. Apart from these traditional applications, large serpentinite reserves have the potential for being used in more sophisticated non-traditional fields. For example, serpentinite can be used for carbon dioxide capture and storage [18,30,11,23], as a potential source of nickel [17] or as a raw material in the production of metallic magnesium and/or pure magnesium compounds [3,10,29,22]. Its potential in wastewater remediation has not been estimated yet.

Various industrial and other human activities produce a large quantity of pollutants that must be removed from the wastewater before they enter aquatic systems. Among the numerous techniques used for treatment of polluted water, adsorption is a promising alternative due to easy handling, low operating costs, and high efficiency for removing very low levels of heavy metals from dilute solutions. Threat of secondary contamination is minimal. Saturated and exhausted adsorbents can be regenerated for reuse or solidified and safely deposited in the appropriate place without the risk of its leaching into environment. There are many adsorbents that can be used for removal of heavy metals and other pollutants from aqueous solutions including oxidized carbon nanotubes [31], activated carbon [20], templated mesoporous carbon [21], clay and alumosilicate based composites [27,26,25], biomass sources [4], clinoptilolite [19], etc. Recently, interesting studies on Cd adsorption onto attapulgite [13] and montmorillonite [33] were reported.

However, it could be noticed that adsorption very often implies a certain extent of the exchange of electrons or at least minimal interaction of electron clouds between the adsorbent active centers and adsorbate. A special case is when the material has a distinct electrochemical activity and allows the pollutant to be oxidized or reduced and then deposited on the surface or into the porous medium of electrochemically active material [27]. Such materials possess discrete clusters, layers or aggregates with non-stoichiometric composition, i.e. metal excess, which provides free electrons available for spontaneous reduction processes in water. However, very little attention has been devoted so far to composite materials that have these properties. Basically, they have inert matrix whose properties have been modified by the addition of selected dopants thus causing its increased activity and electrical conductivity. Within modified matrix, discrete clusters, layers and aggregates can be incorporated or formed, which are responsible for the pronounced electrochemical activity [7,8]. For this reason, examination of electrochemical characteristics of a material has a certain merit for its application in the removal of heavy metals from water. Serpentinite is a very abundant natural material which adsorption and electrochemical characteristic as well as its potential for electrochemically active composite preparation have not been thoroughly examined so far.

Composite based carbon paste electrodes (CPE) are widely used electrodes in the fields of electrochemistry, due to their attractive advantages, such as low-cost implementation, simple preparation, low background current and wide potential window [28]. The most commonly used materials for CPE preparation are commercial graphite powders which are mixed with suitable binder (“pasting liquid”) to form a homogeneous paste [2,9].

This complex study concerns morpho-structural, adsorption and electrochemical characteristics of natural serpentinite from southern Serbia. Adsorption characteristic of natural serpentinite was investigated toward selected organic and inorganic pollutants: Cd^{2+} and anionic textile dyes (Procion red MX-5B, Procion orange and Ramazol black). The scope concerning adsorption was directed to reliable and high-efficient removal of hazardous Cd^{2+} from the solutions with concentrations of up to 200 $\mu g/dm^3$ and anionic dyes from concentration of 100 mg/dm^3, during relatively short contact times (15 or 30 min). Short contact times were chosen in order to evaluate potential application of raw serpentinite as adsorbent in columns for water purification in real systems. Additionally, serpentinite was modified through magnesium impregnation and thermal treatment leading to formation of forsterite which were both electrochemically examined for potential applications.

To the best of our knowledge, there is no publication regarding electrochemical characterization of serpentinite and forsterite as electrocatalytic materials for carbon paste electrode. Both serpentinite and forsterite have been investigated by cyclic voltammetry measurements using modified carbon paste electrode (MCPE) in solution of 0.1 M H_2SO_4 as acidic supporting electrolyte, within potential range from −1 V to 1.7 V vs Ag/AgCl (saturated KCl) reference electrode. In addition, 1 mM $K_4[Fe(CN)_6]$ was used as a redox model compound. Parallel examinations were conducted with carbon paste electrode (CPE), containing only graphite and pasting liquid.

2. Materials and methods

2.1. Preparation of samples

The samples used in the present study originated from the mountain Kopaonik in southern Serbia. They were collected at the surface of ground as irregularly shaped rocks with sharp edges and non-uniform sizes (diameter 5–10 cm). In order to avoid variations in rock composition, representative sample weighing 0.5 kg was crushed to a grain size of less than 3 mm. Subsequently, it was ground to obtain a fine grained powder. Final sample of natural serpentinite was grinded in agate mortar and sieved through 100 mesh sieve. The obtained powder was used for further examinations and preparation of forsterite, according to the following procedure. Quantity of 10 g of powdered serpentinite was mixed with 10 cm^3 of 100 g/dm^3 $Mg(NO_3)_2$ aqueous solution and heated at 80 °C under vacuum. After that, the obtained product was transferred onto glass, dried at 140 °C and than heated in ceramic crucible with rate of 10 °C/min to temperature of 900 °C which was maintained during the next 30 min. The material was spontaneously cooled down to room temperature, powdered in agate mortar, passed through 100 mesh sieve, and used for the experiments.

2.2. Characterization

The morphology of the materials was investigated by scanning electron microscopy (JEOL JSM 5300). For the crystalline characterization, the samples were analyzed at room temperature by X-ray powder diffraction (XRPD) using Ultima IV Rigaku diffractometer, equipped with Cu $K\alpha_{1,2}$ radiation source. The electrochemical properties of the serpentinite and forsterite were evaluated using cyclic voltammetry (CV) of 0.1 M H_2SO_4 and 1 mM $K_4[Fe(CN)_6]$. Working solutions were prepared daily. Deionized water was supplied from Millipore purification system (Bedford, MA, USA). Voltammetric measurements were carried out in a glass electrochemical cell at 22 °C. Prior to measurements, 10 cm^3 of the solution was purged with nitrogen for 5 min. Electrochemical measurements were performed using 797 VA Computrace analyzer (Metrohm) controlled by 797 VA Computrace software version 1.2 for all voltammetric measurements. A three-electrode system was used including MCPEs as the working electrode, Ag/AgCl electrode (saturated with KCl) as the reference electrode, and platinum wire as the auxiliary electrode.

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