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TESTING SORPTION PROPERTIES OF HALLOYSITE BY MEANS OF THE LASER INTERFEROMETRY METHOD

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The objective of the present study has been to test the laser interferometry method in terms of its usability for investigating sorption properties of minerals. This method was used to test the absorption capacity of halloysite with reference to glucose, which is often found in industrial wastewater and whose excess can disturb the environmental eco-balance. The sorption capacity of halloysite was thus determined indirectly, basing on the comparison of concentration profiles as well as time characteristics of glucose quantities released from the control solution and from the solution incubated with a halloysite adsorbent. An analysis of glucose diffusion was conducted in a two-chamber membrane system. On the basis of the obtained concentration profiles, the evolution of the concentration field was determined; so were the removal efficiency (%) and the amount of glucose adsorbed at equilibrium (q_e, mg/g). The obtained results confirm good sorption properties of halloysite with respect to the investigated substance as well as usability of the method for this kind of investigations. The presented tests suggest that the measurement set-up can be optimised in such as way that visual rendering and testing the kinetics of the adsorbed substance direct release from the studied material become possible.

INTRODUCTION

Minerals from the kaolinite group, including halloysite, have the capacity to easily adsorb various substances from water solutions. Due to this, they are used as sorbents, molecular sieves, organic-mineral hybrid materials and ion exchangers. Their sorption properties are the subject of numerous scientific studies in which a variety of methods are used such as UV-vis spectrophotometry (Jamil *et al*.,2011; Liou *et al*., 2011). Halloysite is used as an adsorbent for many various substances (Liou *et al*., 2011; Viseras *et al*., 2008; Del Rey-Bueno *et al*., 1989; Mellouk *et al*., 2009; Wang *et al*., 2010), as well as for incapsulation of biologically active molecules, such as biocides and medicines (Veerabadran *et al*., 2007, 2009; Abdullayev *et al*., 2009). This study shows the results of research into sorption properties of halloysite with respect to glucose which is often found in the wastewater produced by food and textile industries. Sugars are non-toxic substances, yet their excess can upset the environmental eco-balance, particularly on the microscale (e.g. by influencing the bacterial flora).

The test results have been obtained by means of an original measurement technique, based on laser interferometry (Lerche, 1976). It enables complex study of substance diffusion processes in solutions and the evolution of the concentration field by means of determination of gradients and spatio-temporal distribution of concentrations, and in particular – the visual rendering of formation and evolution processes of concentration boundary layers (CBLs), together with measurement of parameters characteristic thereof (Shaposhnik *et al*., 1998, 2008) . The technique proposed below has already been successfully applied in quantitative analysis of ethanol, glucose and sucrose transport through nucleopore and cellulose membranes (Dworecki, Ślęzak & Wąsik, 2003; Ślęzak *et al*., 2005; Dworecki *et al*., 2005, 2006; Wąsik *et al*., 2010). Moreover, the modification of the laser interferometry technique by immobilising the tested molecules in agarose gel and measuring the amount of released substances, used by our team, has enabled determination of the interactions within partially insoluble mixtures, such as the lipopolisaccharide (LPS)-colistin (Arabski *et al*., 2007), LPS-chitosan (Arabski *et al*., 2009a) or LPS-saponin (Arabski *et al*., 2009b).

The presented results of the study into halloysite are of pilot character and confirm the effectiveness of the laser interferometry method as a new method of testing sorption properties of minerals.

MATERIALS AND METHODS

Laser interferometric set-up

The sorption properties of halloysite have been determined experimentally on the basis of a comparison between the quantity of the substance released into pure water from the control solution and from the solution incubated with halloysite. The scheme and detailed description of the interferometric measurement system, used in this experiment, have already been presented in our papers (Dworecki *et al*., 2003; 2006). The system consists of a two-beam Mach-Zehnder interferometer with an He-Ne laser, a membrane system, a TV-CCD camera, and a computer with software for the acquisition and processing of interference images (interferograms). The membrane system under discussion consists of two glass cuvettes (internal dimensions: 70 mm high, 10 mm wide, optical path length: 7 mm), separated by the horizontally located cellulose membrane (*Nephrophane*). The thickness of this membrane is l=16±2 μm and its permeability for glucose $\omega_m=8\cdot10^{-9}$ mol $N^{-1}s^{-1}$. The cuvettes are made with optical glass of high uniformity. The lower cuvette was filled with the solution while in the upper one there was pure water.

The interferograms, which appear due to the interference of laser beams, are determined by the refraction coefficient of the solute which in turn depends on substance concentration. When the solute is uniform, the interference fringes are straight and they bend when a concentration gradient appears. The concentration profile $C(x,t)$ is determined by the deviation $d(x,t)$ of the fringes from a straight course. Since the concentration $C(x,t)$ and the refraction coefficient are assumed to be linear (Dworecki *et al*., 2003; 2005, 2006), we have:

$$C(x,t) = C_0 + a\frac{\lambda d(x,t)}{hf}, \qquad (1)$$

where $C(x,t)$ denotes the concentration of glucose at a point situated at the distance x from the membrane-water interface; C_0 is the initial substance concentration; a is the proportionality constant between the concentration and the refraction index (a=33.05×10^3 mol/m^3 for the glucose aqueous solution); λ is the wavelength of the laser light 632,8 nm; h is the distance between the fringes in the field where they are straight lines; and f is the thickness of the solution layer in the measurement cuvette.

The amount of glucose $N(t)$, which diffuses in the time t from the solution to water was calculated by integrating the concentration profile according to:

$$N(t) = S\int_0^{\delta} C(x,t)dx, \qquad (2)$$

where S is the surface of membrane (S=7×10^{-5} m^2), and δ is the CBL thickness.

The values C (x,t) and δ were determined experimentally with the use of interferograms (Figs. 1AB), obtained by the laser interferometry system with the use of the software for interference images processing. The CBL thickness δ was defined as the distance between the membrane-water interface and the point at which the deviation of the interference fringe from its straight line run amounts to 10% of the fringe thickness (Dworecki *et al*. 2006). By recording the interferograms over a given time interval one can reconstruct the concentration profiles at different times. The interferograms were recorded from 120 to 2400 s with a time interval of Δt = 120 s and the concentration profiles for each interferogram were reconstructed. Such profiles were used to calculate the amount of glucose (mol) transported through the membrane in a function of time ($N(t)$).

Research methodology

For the purposes of the present study, halloysite which originated from the Dunino open pit mine in Silesia (Poland) was used. The halloysite was sieved through a sieve (mesh diameter 0.25 mm) in order to be cleansed of clayey residues. Then it was preliminarily rinsed with tap water, which removed contamination with particulate matter. The clay mineral was rinsed five times with distilled water and stirred with a magnetic stirrer for 15-20 minutes in order to remove the remaining mine contamination and ions adsorbed from tap water. A sample of 250g of drained halloysite was weighed and then digested with the 40% sulphuric acid over 60 minutes. During sample digestion with the acid, the magnetic stirrer was stirring at the temperature of 40-50°C. The obtained solution was decanted; the halloysite was rinsed three times with distilled water and dried at the temperature of ca. 100°C. Next, the weight m=0.5 g of halloysite was rinsed three times with doubly deionised mili-Q and then sterilised (30 mins., 121°C, 1.08 bar). Following sterilisation, the sample was centrifuged (15 mins., 5000 rpm), and to the halloysite sediment was added V=1 ml of glucose solution of concentration C_0=0.05M in doubly deionised mili-Q water. The sample was incubated for 18 hours at the temperature of 22°C; the suspension was then centrifuged (30 mins., 12,000 rpm) and the supernatant was decanted for an interferometric analysis. The control sample is constituted by a 0.05M glucose solution. The experiments were performed at the temperature of 20°C.

RESULTS AND DISCUSSION

In Figs. 1AB, selected interferograms obtained for control (A) and incubated (B) solution are presented. The interferometric fringes give essential information about the glucose concentration distribution inside the measuring system. The right bending of the fringes in the upper cuvette reflects the increase of glucose concentration, and the left bending of these fringes in the lower cuvette indicates a decrease of glucose concentration in the near membrane region. The comparison of the interferograms (A) and (B) clearly shows that the fringes for the control solution are more bent than those for the incubated solution, which indicates higher concentration shift for the control solution.

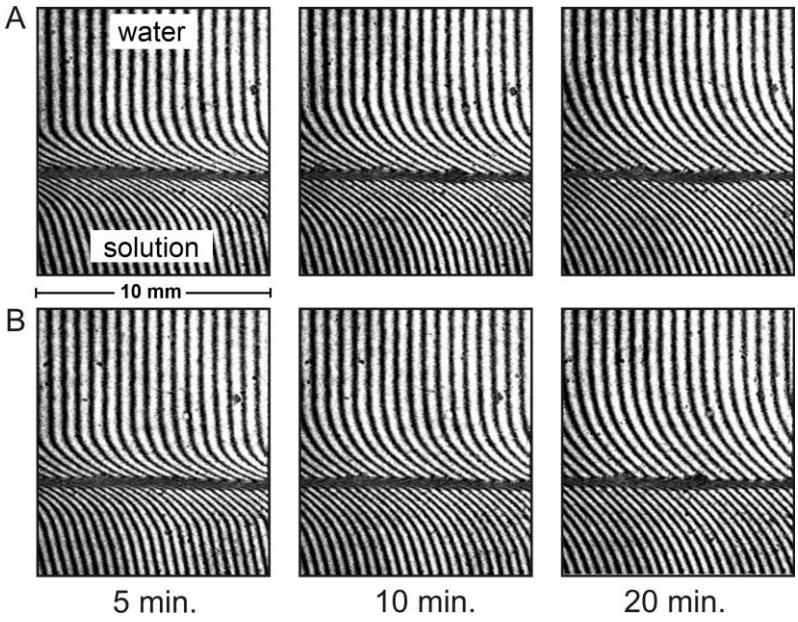

Fig. 1. Selected interferograms obtained after times of 5, 10 and 20 mins. for control (A) and incubated (B) solutions.

Fig. 2 presents the concentration profiles obtained on the basis of a computer analysis of the interferograms shown in Figs. 1AB. As can be seen, the values of $C(x,t)$ for the control solution are higher than for the incubated solution.

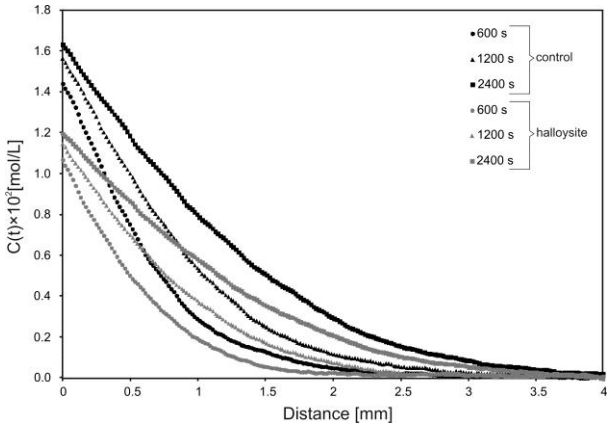

Fig.2. Concentration profiles obtained for the control glucose solution (output concentration 0.05 M) and the incubated solution with halloysite for times of 600s, 1200s and 2400s.

The $C(x,t)$ values are linear dependent on the initial concentration (C_0) of solution (Eq. 2).

So the shift in concentration profiles indicates lower initial concentration of the solution after incubation. One of the possibilities offered by the interferometric method is determination of concentration evolution at any point.

Fig. 3 shows evolution of the concentration field at points situated at distances of 0, 0.5, 1 and 2mm away from the membrane surface.

The highest changes to concentration are observed on the membrane surface. Yet at each point within the CBLs area, the concentration in the case of the incubated solution is lower than in the control solution, e.g. on the membrane surface after 40 mins (in stationary state) the concentration amounts to 1.19×10^{-2} M for the incubated solution and 1.63×10^{-2} M for the control solution respectively.

Fig. 4 shows the curves for glucose release from the control and incubated solutions, obtained on the basis of the correlation (1) and the reconstructed concentration profiles. These curves follow typical courses (Dworecki *et al*., 2005, 2006).

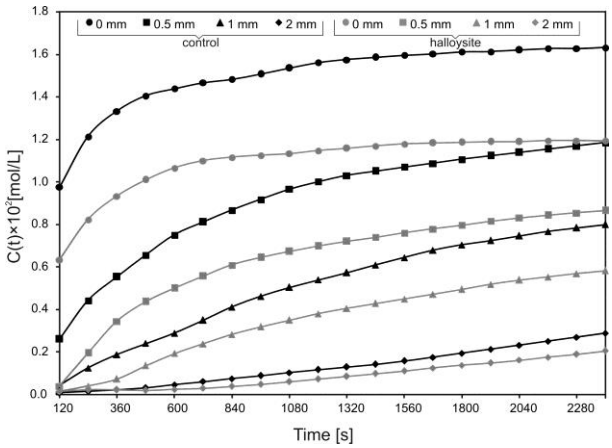

Fig.3. Time evolution $C(t)$ of the concentration field at points situated 0, 0.5, 1 and 2 mm away from the membrane for the control solution and the incubated solution with halloysite.

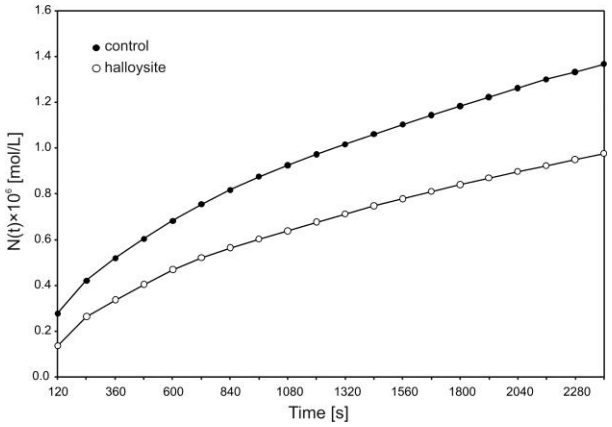

Fig.4. Time characteristics for glucose release from the control solution and following incubation with halloysite.

The amount of glucose released from solution grows non-linearly in time due to polarisation of the membrane system. As already indicated, the quantities $C(x,t)$ are proportional to the output concentration of the solution (C_0); hence, according to the correlation (2), the quantity of the substance released from the solution is also proportional to that concentration. From Fig. 4, it follows that the quantity of glucose released from the solution incubated with halloysite accounts for ca. 67% of the quantity released from the control solution. This means that the concentration of the glucose solution after 18 hours of incubation with halloysite at equilibrium decreases from C_0=0.05M to C_e≅0.033M, which remains in accordance with the data in Figs. 2 and 3.

The removal efficiency (%) and the amount of glucose adsorbed at equilibrium (q_e, mg/g) were calculated according to the formulas (2):

$$Removal(\%) = \frac{(C_0 - C_e)}{C_0} \times 100$$

$$q_e = \frac{(C_0 - C_e)V}{m}$$

and the following values were obtained, respectively: removal efficiency ≈ 34%, q_e ≈ 6.12mg/g (=3.4×10^{-5} mol/g).

CONCLUSIONS

The conducted study has confirmed good sorption properties of halloysite with respect to glucose and its usability as an adsorbent of unwanted organic substances contained in industrial waste and wastewater. The above study is of pilot nature and one of its major objectives has been to test the effectiveness of the interferometric method as a new and practical technique in testing sorption properties of minerals. In this study, the sorption capacity of the halloysite adsorbent has been determined indirectly, basing on the quantity of the substance released from the solution incubated with halloysite. In future, we intend to optimise the method in such a way that a visual rendering and a study of removal kinetics of the adsorbed substance directly from the granular halloysite can be made.

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