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HOLOGRAPHIC INTERFEROMETRY USING PHOTOREFRACTIVE CRYSTALS FOR MASS TRANSFER PROCESSES INVESTIGATION

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This paper extends the applications of holographic interferometry by four wave mixing using photorefractive crystals to the study of mass transfer processes such as interfacial turbulence (Marangoni effect) and adsorption. The recording material, a $Bi_{12}TiO_{20}$ crystal, has good sensitivity and diffraction efficiency at the wavelength of the laser diode used as light source, even without external electric field applied on the crystal, unlimited reusability and allows the control of the writing and storage times. Interfacial instabilities produced by Marangoni convection driven by surface tension gradient can intensify the efficiency of various separation processes but are far from being understood completely, so the experimental studies are very important in order to predict a stability criterion. We have studied some liquid – liquid systems characterised by an intense interfacial turbulence induced by the acetic acid. In order to characterise the adsorbent properties of adsorbent materials, it is necessary to determine the concentration profile in the vicinity of the adsorbent. We studied phenol adsorption on granular activated coal and powder activated coal. The visualisation of the diffusion layer and measurements of its dynamics have been performed.

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1. Introduction

Among the most important applications of holographic interferometry (HI) are those concerning phase objects study, i.e. transparent media presenting refractive index inhomogenities. Holographic interferometry of phase objects is widely used in studies and experiments in aerodynamics, plasma diagnosis, optical testing, holographic photoelasticity, heat and mass transfer phenomena.

The powerful technique of HI has been used in chemical engineering, for instance, for accurate measurements of diffusion coefficients, for the visualisation of several mass and heat transfer phenomena and also for computing of local mass and heat transfer coefficients.

Real-time HI was strongly stimulated by the progress in physical and technology of photorefractive crystals (PRC) as reusable holographic materials that can be infinitely recycled and do not require additional processing. The erasure can be achieved optically by uniform illumination of the crystal.

Double-exposure and time-average HI in $Bi_{12}SiO_{20}$ (BSO) and $Bi_{12}GeO_{20}$ (BGO) crystals were successfully demonstrated by Huignard et al. in four-wave mixing (4WM) configuration [1,2].

We have studied real-time HI in $Bi_{12}TiO_{20}$ (BTO) crystals using 4WM configuration [3], Dainty and Troth [4] studied HI using anisotropic self-diffraction in BSO, Magnusson et al. [5]

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studied HI in lithium niobate, Dirksen and Bally [6] - real time HI in sillenites and Georges and Lemaire [7] - phase shifting real-time HI in BSO.

This paper extends the applications of HI using PRC to the study of mass transfer processes such as interfacial turbulence (Marangoni effect) and adsorption. Marangoni convection driven by surface tension gradient often accompanies mass or heat transfer in liquid-liquid and liquid-gas systems, and can intensify the efficiency of various separation processes like distillation, absorption and extraction. Interfacial instabilities are far from being completely understood, so experimental studies are very important.

We performed real-time and double exposure HI on BTO crystals in 4WM configuration with low-power laser diode. The four wave mixing configuration chosen for the interferometry setup proved some advantages upon the classical one: the reconstructed image is not any more superimposed on the direct one, seen by the TV camera, and the phase distortions introduced by the crystal are corrected by phase conjugation leading to better quality and low noise interferograms. The life-time of holographic interferograms in PRC, with continuous read-out and captured by a TV camera, was compatible with the acquisition time of the PC image acquisition and processing system. This is the meaning of “real-time” in this paper. The holograms life-time is correlated with the time scale of the object evolution, which can be of the order of magnitude from seconds to tens of minutes (using c.w. lasers). There is a wide class of complex phenomena (physical, chemical, biochemical), which evolve at this time scale, for instance, diffusion of proteins, diffusion of drugs in the blood circuit, some multi-phase flows, crystal growth (particularly in microgravity conditions). The spatial behaviour of these complex phenomena is very sensitive to the boundary conditions and therefore their numerical modelling needs information on these spatial conditions and on the approximate spatial form of the solutions. This information can be obtained by “real-time” HI, in particular with a simple, compact, low-power and inexpensive holographic interferometer, as demonstrated in this paper.

2. Experimental setup

The visualising and measuring method used in this paper is real-time and double-exposure interferometry using a BTO photorefractive crystal. Classically, HI with double exposure implies the recording of two different holograms of the studied object in the same holographic recording material. The hologram of the first object state is recorded and simultaneously read-out up to the moment t_0. After this moment, the object state changes. At the moment t_1 a hologram of the second state of the object starts to be recorded, producing the partial erasure of the first one. Thus, the holograms of both states of the object exist in crystal for a certain time and they can be read-out simultaneously. The reconstructed images yield an interference pattern, which represent planes of the same refractive index. When mass transfer processes in fluid phase are studied, these planes are iso-concentration ones.

In this paper, we have visualised interfacial mass transfer (interfacial turbulence) of the acetic acid in some systems and we have studied the phenol adsorption in different types of active coal, investigating its dynamics by measuring the thickness of the diffusion layer.

The holographic interferometer was implemented in the compact 4WM configuration (Fig. 1).

This setup allows testing of transparent liquids (in red light) with optimum image quality. A laser diode (SDL 7501) was used as light source ($P = 10$ mW, $\lambda = 633$ nm). The image of the object plane is produced by the objective OB1 ($f = 150$ mm) in plane I1. The size of this image is matched to the size of the CCD matrix of the TV camera (TVC). The objective OB2 ($f = 50$ mm) further images the object plane I1 inside the BTO crystal ($6 \times 8 \times 8$ mm) (plane I2), as signal beam. The optical surfaces of the BTO crystal were parallel to the (110) crystallographic planes. Without external field (high voltage) applied on the crystal, the recording of holograms on sillenite crystals is mainly yielded by the diffusion of free charge carriers. The diffraction efficiency is increasing with the increase of the mean spatial frequency of the hologram. In the holographic interferometer we set-up, the angle between the object and reference beams is 50° and the ratio object beam/pump beam is 1/30 for 300 mW/cm^2 laser light intensity. In this case, the diffraction efficiencies without and with external field are close enough, justifying the hologram recording without an additional high voltage external field applied on the crystal. The pump beams are P1 and P2. The conjugated beam S* (the beam produced by the reading of the holographic interferogram), back reflected through OB2, is extracted by the beam splitter BS2 and imaged on the CCD matrix of the TVC (without objective). This image is acquired by a PC with an acquisition board. In order to enhance the signal-to-noise ratio, a polariser is placed in front of the TVC.

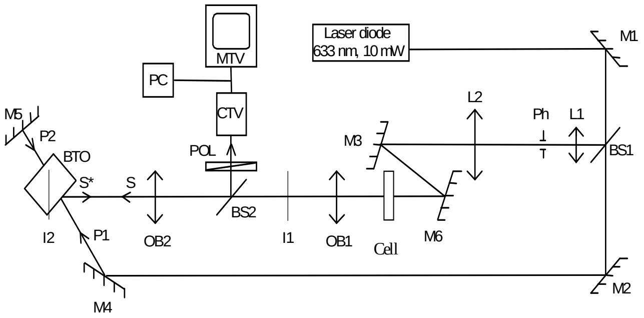


Fig.1. Holographic interferometer using four – wave mixing in photorefractive BTO crystal.

3. Experimental results and discussion

3.1. Interfacial instabilities

Interfacial dynamic instabilities, with self-amplifying and self-organising convection driven by interfacial tension, have been observed in many fluid - fluid systems with and without chemical reactions [8 - 11]. Because intensive convective flows driven by interfacial tension gradients lead to important increase of mass transfer rates, interfacial turbulence seems to be a good way for enhancement of separation processes as recovery of crude oil [12] and of metallic ions from waste water [13], for example. Several other optical techniques have been used to investigate the interfacial instabilities. Observation of cellular convection in systems in which interfacial turbulence occurs were made using schlieren technique [14, 15], laser-activated photochromic tracer techniques [16], microscopic observations in reflected or transmitted light or micro-interferometry and Mach-Zehnder interferometry [17].

In order to show that real-time HI by 4WM on BTO crystals is a fast and simple optical method to investigate the interfacial turbulence, we have studied three ternary systems (Table 1) which are known to exhibit the interfacial turbulence in well-defined conditions.

Table 1. Ternary systems studied.

Phase 1	Phase 2	Solute
water	n-butyl acetate	acetic acid
glycerol	n-butyl acetate	acetic acid
chloroform	water	acetic acid

HI by 4WM for the first studied system, water - n-butyl acetate - acetic acid, was previously reported by us [18]. In this case, the interferograms show a deformation of interference fringes when cellular convection accompanying mass transfer occurs. We consider that this deformation can be associated with surface tension gradients. These gradients induce a flow in the plane of the interface, supplied by fresh fluid from the bulk.

The second studied system, glycerol - acetic acid - n-butylacetate, was observed with an optical microscope in transmitted light (Fig. 2a - c) before studying it by HI. These observations allowed us to find out the proper concentrations of the liquid components for a convenient temporal evolution of the interfacial turbulence process, related to the time scale of our recording system.

When glycerol - acetic acid system is put in contact with n-butylacetate, the interface becomes instantaneously unstable. In Fig. 2a is presented a photograph in which are visible the regions in the vicinity of the interface with an incipient cellular organisation. The system glycerol - acetic acid - n-butylacetate exhibits organised interfacial activity upon transfer of acetic acid from the glycerol phase to the acetate phase. The concentration of acetic acid necessary to observe cellular activity was found to be between 0.63 g/l – 1.27 g/l. In our experiment we used 127 g/l acetic acid in glycerol. For this concentration, Orell and Westwater [15] reported unusually large cells that propagate at relatively low speed. In Fig. 2b and 2c are presented images of the deformed interface due to interfacial mass transfer.

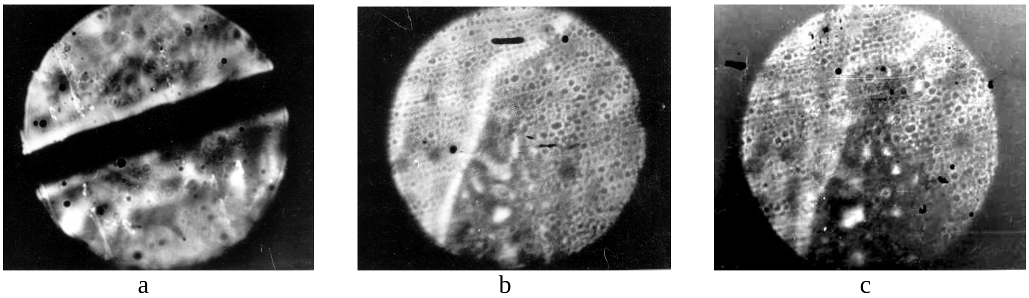


Fig. 2. Microscope photographs showing interfacial turbulence in the system glycerol – acetic acid – n-butylacetate.

For the interferometric investigation, a transparent cell with optical quality windows was half-filled with a solution of acetic acid in glycerol, with the concentration in the range determined by microscope observations, and a comparable volume of n-butylacetate has been added. In Fig. 3a - c are shown interferograms obtained at different times for this system, using the experimental setup presented in Fig. 1.

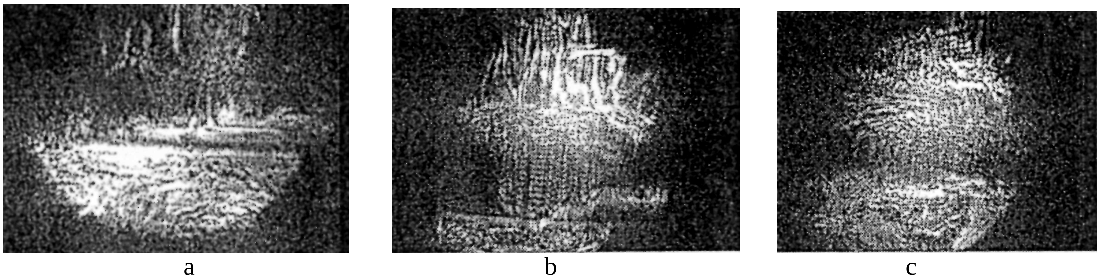


Fig. 3. Interferograms showing interfacial turbulence for the system glycerol – acetic acid – n-butylacetate at different times: a) 10 sec; b) 40 sec; c) 60 sec.

All changes in fringes shape are due to the variation of the refractive index that is related with the change in concentration profile. In this case, diffusion and convection due to interfacial turbulence control the overall mass transport. The position of the interface between the components, after 10 sec, when the turbulence is in an incipient stage, is in the middle of the Fig. 3a (the black continuous line). When the interfacial turbulence is developed, the interface position and shape are continuously and rapidly changing and it is almost impossible to specify its instantaneous position.

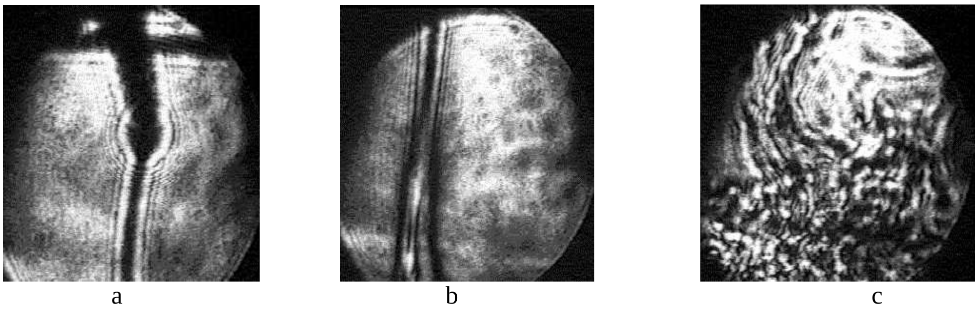


Fig. 4. Interferograms obtained for drops of acetic acid – chloroform in water: drop forming, a) and drop falling, at 1 cm from the nozzle; b) and at the bottom cell, c).

The third system chloroform - water - acetic acid was studied in two cases. In the first one, the organic solution chloroform - acetic acid was dropped in water using a syringe. Acetic acid was transferred from chloroform to water, which was initially free of solute. In Fig. 4 are presented interferograms for a drop of acetic acid - chloroform solution (105 g/l concentration) in water. In the absence of acetic acid we have not obtained interference fringes. During drop formation (Fig. 4a) it can be observed that an emulsion is formed due to the mass transfer. This is a consequence of the interfacial turbulence that is often encountered when acetic acid is transferred from organic to aqueous solutions [10].

In the second case, the chloroform was dropped into an acetic acid – water solution. The acetic acid was transferred from water to chloroform. In Fig. 5 are presented interferograms of this system for a concentration of acetic acid in water of 52 g/l (a, b) and 70 g/l (c).

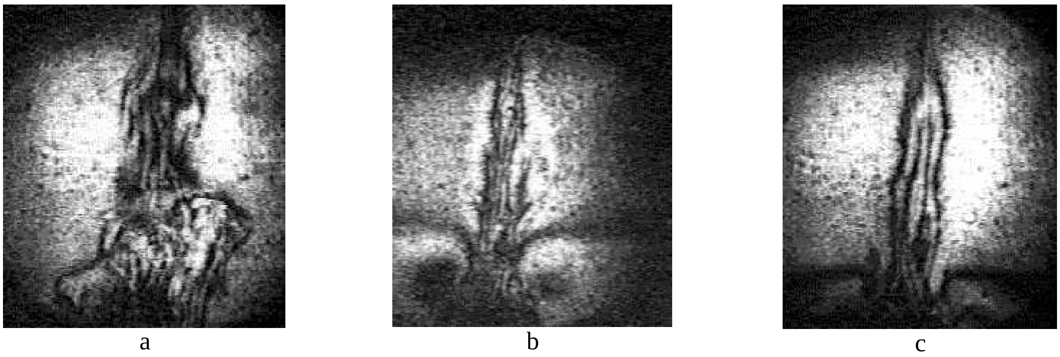


Fig. 5. Interfacial turbulence of acetic acid from a water solution into a chloroform droplet: system evolution for 52 g/l concentration of acetic acid in water, at two moments, a) 3 sec and b) 5 sec; c) system observation for 70 g/l concentration of acetic acid, at 2 sec.

3.2. Phenol adsorption

Among the purification technologies, adsorption is widely used in ecological procedures for chemical industry, for water and air purification. The study of adsorbent properties of different materials is very important because there are a lot of adsorbent materials that have been insufficiently studied till now. Due to the complexity of the phenomenon, in order to check-up the adsorbent properties of different materials it is necessary to determine the modelling parameters, diffusion constant and the concentration profile in the vicinity of the adsorbent.

We have chosen to study phenol adsorption because phenol is a major pollutant under strict effluent restriction, which is imposed to petro-chemistry and coal industry. Its toxicity is well known, both in aquatic environment and human health. Phenol and phenol substitutes are extremely toxic to aquatic bio-system and impart a strong and disagreeable odour. The main sources of phenol in wastewater are the industries such as petrochemical, hydro-desulfuration of flue gas, catalytic hydrogenation, coal gasification, pesticide manufacture and electroplating and metallurgical operations. The concentration of phenol in wastewater streams is often much higher than international regulations (0.001ppm) and that is why it is necessary a permanent and efficient control. As adsorbent materials we used granular activated coal (GAC) and powder activated coal (PAC) because their properties recommend them not only for phenol adsorption, but also for a broad range of organic and inorganic compounds. Column adsorber packed with GAC is used to treat ground water and industrial wastewater contaminated with organic compounds. To properly design a GAC column, information regarding adsorption equilibrium and kinetics are required. Equilibrium data can be easily collected from batch experiments. On the other hand, accurate kinetic data including film transfer rate and interparticle diffusion rate parameters are more difficult to obtain.

We have found that the compact 4WM configuration of the holographic interferometer from Fig. 1, is proper for the visualisation of the diffusion layer and measurements of its dynamics.

The interferograms shown in Fig. 6 a-b are due to phenol adsorption on GAC placed in a bottom corner of the cell. The phenol adsorption determines a variation of the density of the aqueous solution in the vicinity of the GAC that generates, by free convection, a movement of the liquid in the vicinity of GAC. To describe the two superimposed processes (free convection and diffusion) involved in this complex mass transfer process, the mathematical formalism implies the simultaneous solving of Navier-Stokes equations and the concentration field equation [17]. An analytical solution of these equations does not exist up to now. Numerical solving of this equation system can lead to the spatial and temporal concentration distribution in the aqueous solution, but it is very sensitive to the boundary conditions. This distribution could be visualised and studied more conveniently by HI using 4WM on PRC that allows rapid and easy changing of the boundary conditions and absorbents.

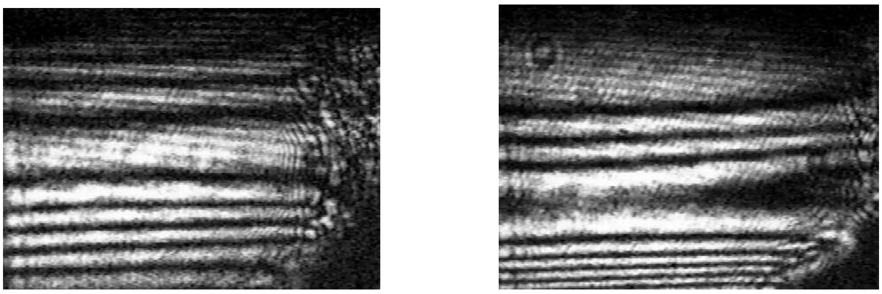

a b

Fig. 6. Holographic interferograms of phenol adsorption at 3 min (a), 5 min (b). The GAC is placed in the right bottom corner of the cell.

In Figs. 7 and 8 are shown interferograms obtained for the two adsorbents, GAC (Fig. 7) and PAC (Fig. 8) disposed on a metallic grid placed on the top of the cell. In this case, in the vicinity of carbon layer, the adsorption and molecular diffusion will appear only. In Fig. 7, the time evolution of the diffusion layer (the layer from which the phenol is adsorbed by the adsorbent) for the adsorption in GAC is shown. The sequence of interferograms was obtained at moments equally separated by 10 min, in the time interval 0-50 min (from the beginning of adsorption).

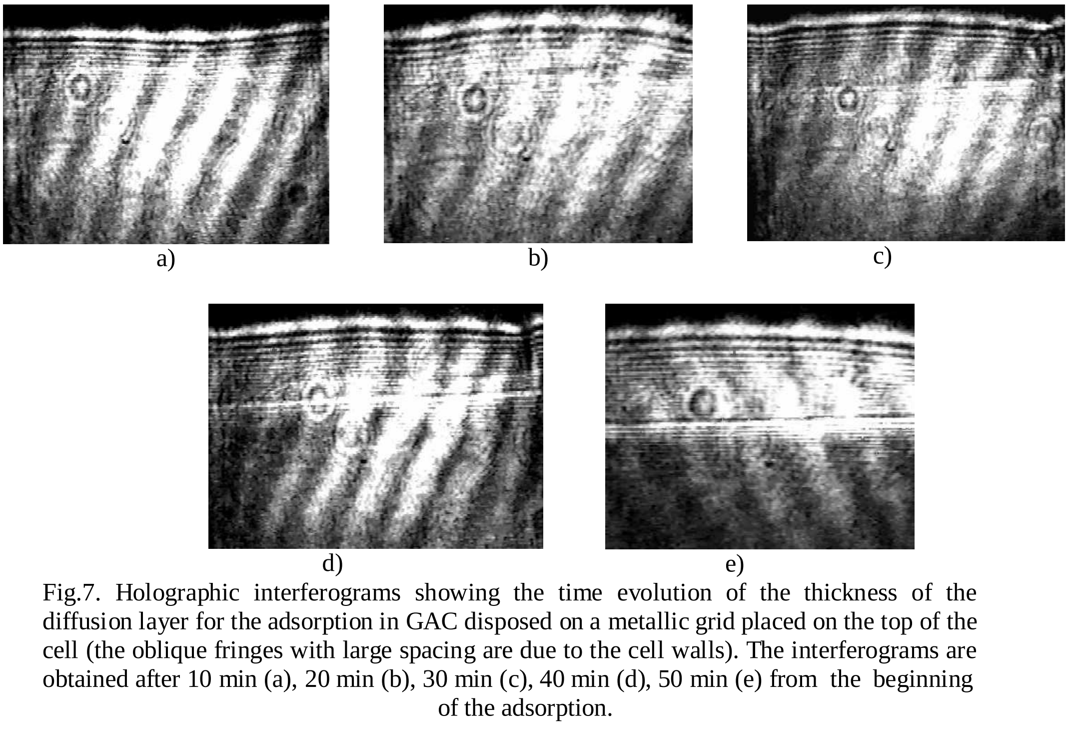
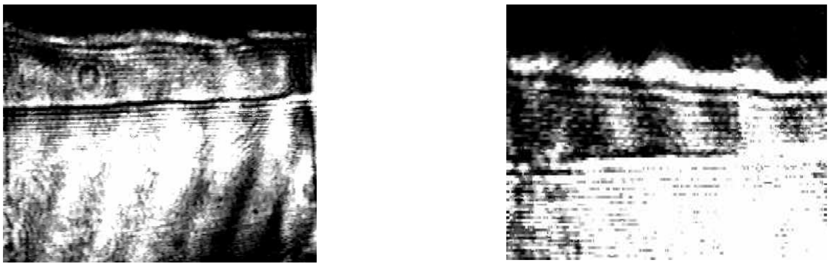

a) b) c)
d) e)

Fig.7. Holographic interferograms showing the time evolution of the thickness of the diffusion layer for the adsorption in GAC disposed on a metallic grid placed on the top of the cell (the oblique fringes with large spacing are due to the cell walls). The interferograms are obtained after 10 min (a), 20 min (b), 30 min (c), 40 min (d), 50 min (e) from the beginning of the adsorption.

In Fig. 8, the time evolution of the diffusion layer for the adsorption in PAC is shown after 20 min and 30 min. Even though the adsorption is more efficient in PAC, the fringe contrast is worse in this case due to the penetration of the small powder granules through the grid that we used.



a) b)

Fig. 8. Holographic interferograms showing the thickness of the diffusion layer for the adsorption in PAC (which is disposed on a metallic grid placed on the top of the cell). The interferograms are obtained after 20 min (a) and 30 min (b), from the beginning of the adsorption.

For measuring the thickness of the diffusion layer, the interferometer was calibrated by placing a calibrating object in the same place as the cell. In Fig. 9, the temporal dependence of the diffusion layer thickness is plotted, using the analysis of the interferograms showed in Fig. 7. As it is expected, the increasing of the diffusion layer thickness is faster at the beginning of the adsorption and diminishes in time due to the depletion of the phenol in the vicinity of the activated carbon.

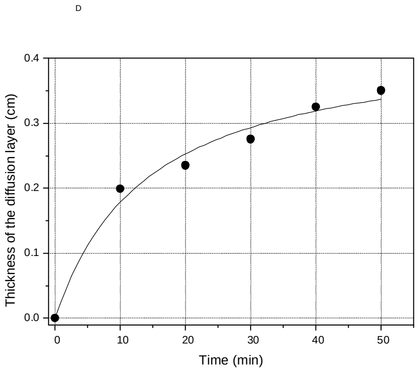


Fig. 9. Dependence of the diffusion layer thickness vs. time, for 45 g/l phenol concentration. Experiment: dots. The solid line is an eye-guide only.

4. Conclusions

there was presented an experimental study of interfacial turbulence and adsorption, and complex mass transfer phenomena without a complete theoretical description up to now, using holographic interferometry by four wave mixing on $Bi_{12}TiO_{20}$ photorefractive crystals. The intense interfacial turbulence induced by the acetic acid in different liquid-liquid systems was recorded. The phenol adsorption on granular activated coal and powder activated coal was studied and the dynamics of the diffusion layer thickness, an important parameter for the evaluation of the adsorbent materials efficiency, has been obtained.

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