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EVALUATION OF THE SYNERGETIC EFFECT OF PYRENEE SORPTION OF CU(II) IONS BASED ON LANGMUIR-FREUNDLIC MODELING

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Abstract. In this work, $CoFe_2O_4$ ferrite nanoparticles were synthesized via a chemical coprecipitation method. As a preparation of the magnetic fluids, magnetic particles stabilized in the water with surfactant sodium oleate. The size and morphology of the $CoFe_2O_4$ ferrite particles were characterized using Transmission Electron Microscopy (TEM). The magnetic hysteresis loops of the synthesized magnetic fluids were measured, revealing that these types of magnetic fluids exhibit superparamagnetic behavior. Furthermore, the time dependence of the light transmission of the magnetic fluid was investigated under external magnetic fields of 500 and 800 Gauss. Experimental results demonstrated that the light transmission of the magnetic fluids extremely increases at higher values of the external magnetic field.

Keywords: magnetic fluid, colloidal solution, chemical synthesis, liquid carrier, surfactant, light transmission, time dependence.

Magnit suyuqliklarining magneto-optik yorug‘lik o‘tkazuvchanligi

Annotatsiya. Tarkibida 3d-metal elementlari bo‘lgan $CoFe_2O_4$ ferrit nanozarralari kimyoviy usulda sintez qilindi va oliat natriy sirt faol moddasidan foydalangan holda suyuq asosda barqarorlashtirilib magnit suyuqliklar tayyorlandi. Transmission elektron mikraskopdan foydalanib $CoFe_2O_4$ ferrit zarralarining hajmi va morfologiyasi o’rganildi. Sintez qilingan magnit suyuqliklarning magnitlanish gisterezisi olindi va bunday turdagi magnit suyuqliklar superparamagnetizm tabiatiga ega ekanligi aniqlandi. Magnit suyuqlikning nur-o’tkazuvchanligi tashqi magnit maydonning 500 va 800 Gauss qiymatlarida vaqtga bog’liqligi tadqiq etildi. Tajriba natijalari shuni ko’rsatdiki tashqi magnit maydonning yuqori qiymatlarida magnit suyuqliklarning nur-o’tkazuvchanligi yuqori bo’ladi.

Kalit so‘zlar: magnit suyuqlik, kalloid eritma, kimyoviy reaksiya, suyuq asos, sirt aktiv moddasi, nur-o’tkazuvchanlik, vaqt.

Магнитооптическое пропускание света в магнитных жидкостях

Аннотация. Наночастицы феррита $CoFe_2O_4$, содержащие элементы 3d-металлов, были химически синтезированы и стабилизированы в жидкой основе с использованием поверхностно-активного вещества олеата натрия для получения магнитных жидкостей. Размер и морфология частиц феррита $CoFe_2O_4$ были изучены с

помощью просвечивающего электронного микроскопа. Была получена гистерезис намагниченности синтезированных магнитных жидкостей, и установлено, что такие магнитные жидкости обладают суперпарамагнитной природой. Была изучена зависимость оптической проводимости магнитной жидкости от времени при значениях внешнего магнитного поля 500 и 800 Гаусс. Экспериментальные результаты показали, что оптическая проводимость магнитных жидкостей выше при более высоких значениях внешнего магнитного поля.

Ключевые слова: магнитная жидкость, коллоидный раствор, химическая реакция, жидкая основа, поверхностно-активное вещество, оптическая проводимость, время.

Introduction. In recent years, ferromagnetic fluids have emerged as a class of “smart nanofluids” that can be controlled by an external magnetic field. Magnetic fluids are distinguished by a wide range of magnetic, electrical, mechanical, and hydrodynamic properties, which lead to their extensive application in various practical fields [1]. Their applications include targeted drug delivery in biomedicine through hydrodynamic motion in an external magnetic field, cancer therapy via hyperthermia, and magnetic cell separation. Furthermore, the ability to control their optical properties using an external magnetic field enables their use in photonic technologies, such as magnetic field-induced switching, modulation, filtering, and optical magnetic field sensors [2–4].

One of the fundamental properties of magnetic fluids is the capability to modulate the intensity of light passing through the sample using an external magnetic field. This phenomenon is known as magneto-optical transmission, and several researchers have experimentally determined the optical transmission of ferrofluids under the influence of a magnetic field [3–9]. Existing studies indicate that magnetic fluids alter their light transmission depending on the external magnetic field strength and time.

Ferrimagnetic nanoparticles within a magnetic fluid directly magnetization when influenced by an external magnetic field, inducing interparticle dipole-dipole interactions. This process leads to the chain-like aggregation of magnetic nanoparticles aligned along the magnetic field lines [4]. Consequently, this phenomenon induces significant modifications in the optical properties of the magnetic fluid medium.

The ability to modulate these optical characteristics via an external magnetic field is a fundamental operational principle for various photonic implementations of ferrofluids. These include tunable optical devices, polarizers, optical isolators, and magnetic field sensors [5–9].

Under the influence of an external magnetic field, the formation of predominantly chain-like structures and in certain instances, cluster aggregations enhances optical anisotropy and light scattering processes within the medium. This results in variations in the intensity of the light transmission through the sample. Specifically, the optical transmission would be characterized as a function of both the magnetic field intensity and time. In cases where the magnetic field is applied parallel to the direction of light beam, the optical transmission of the ferrofluid has revealed initially decrease and subsequently increase [7–13]. Notably, even within the same sample, both reducing and increasing of the light transmission value can be observed depending on the applied magnetic field strength [4].

The temporal evolution of magneto-optical transmission in magnetic fluids is directly governed by the orientation rate of the magnetic nanoparticles, structural reorganization processes, and thermal relaxation mechanisms. Therefore, investigating the time-dependence of transmission

provides a deeper insight into the dynamic characteristics of magneto-optical processes and enables the assessment of structural transitions in magnetic fluids via optical diagnostics. In the present work, the time-dependent optical transmission of a magnetic fluid under two values of the external magnetic field was experimentally investigated. The obtained results elucidate the formation mechanisms of magneto-optical effects and demonstrate the potential for precise control over the optical properties of magnetic fluids.

Methods. Preparation of $CoFe_2O_4$ based Magnetic Fluid. The magnetic fluid was prepared by initially synthesizing $CoFe_2O_4$ nanoparticles. In current study, the ferrimagnetic nanoparticles were synthesized using the chemical co-precipitation method. Metal nitrate salts, specifically $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, were used for preparation. Initially, the metal nitrate salts were taken in a molar ratio of Co^{2+}: Fe^{3+} = 1 : 2 and each was dissolved separately in 100 ml of distilled water. The resulting solutions were stirred for 30 minutes at 60 °C using a magnetic stirrer. Subsequently, the solutions were filtered and combined into a single vessel, then thoroughly mixed at a constant temperature of 60 °C. The reaction process was processed under ambient atmospheric conditions. An alkaline solution, consisting of 8 mole sodium hydroxide (NaOH) dissolved in 1 liter of bi-distilled water, was added dropwise to the mixture until the pH value reached 12. The mixture was then heated to 95 °C and maintained under continuous stirring for 30 minutes. During this period, under the influence of temperature, the metal salts are first converted into hydroxide groups, which subsequently transform into ferrites. The chemical reaction equation is as follows:

$$Co^{2+} + 2Fe^{3+} + 8OH^- \Rightarrow Co(OH)_2 \cdot 2Fe(OH)_3 \quad (1)$$

$$Co(OH)_2 \cdot 2Fe(OH)_3 \overset{100^0C}{\Rightarrow} CoFe_2O_4 + 4H_2C \quad (2)$$

The iron particles that settled to the bottom of the vessel were collected by magnetic separation. The vessel was washed several times with distilled water to remove the residual impurities. The precipitated magnetic particles were filtered and sodium oleate – a surface-active agent was added with stirring. The mixture was stirred well at 80 ^{0}C for one hour and sodium oleate-coated nanoparticles were formed according to the following equation:

$$CoFe_2O_4 + C_{17}H_{33}COONa \overset{80^0C}{\Rightarrow} (CoFe_2O_4) \cdot (C_{17}H_{33}COONa) \quad (3)$$

The sodium oleate-coated nanoparticles were dried in an oven at 100 ^{0}C for 12 hours. After drying, the ferrite nanoparticles were added to distilled water and mixed thoroughly with a magnetic stirrer at 80 ^{0}C for 1 hour to prepare magnetic fluid.

Experimental methods. JEM-2100Plus transmission electron microscope (TEM) used to obtain the size and morphology of the magnetic fluid samples. The magnetization hysteresis of the synthesized magnetic fluids was determined using a LIKE SHORE 7404 VSM vibrating magnetometer. The magneto-optical structure shown in Figure 1 was used to study the magneto-optical permeability of magnetic fluids in an external magnetic field.

The magnetic fluid is contained in an optical glass cuvette, which is positioned in the center of the electromagnets. The cuvette dimensions are 9.5 mm × 10.8 mm × 1 mm (beam path). It is illuminated perpendicularly with polarized light from a He-Ne laser (wavelength: 632.8 nm; power: 1 mW). The electromagnet creates a magnetic field along the direction of the light beam. The intensity of the transmitted light is recorded on a photodetector.

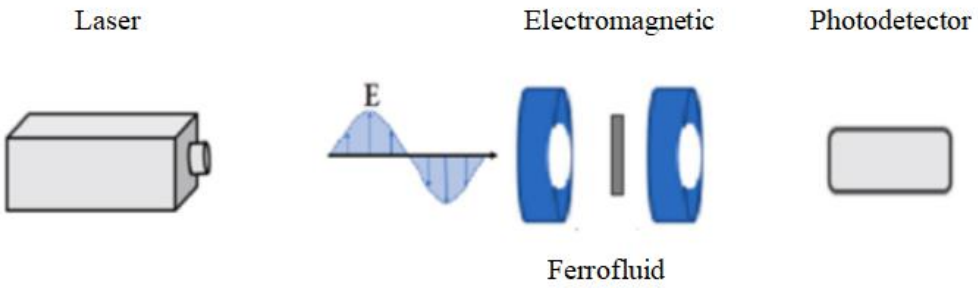


Figure 1. Experimental setup for optical transmission:

The light transmission of the samples is determined by the following formula:

$$T = \frac{I_{B(t)}}{I_0}$$

Here, I_0 is the initial (without a magnetic field) light intensity, and $I_{B(t)}$ is the intensity after t seconds under the influence of the external magnetic field B.

Results and Discussion. The size and morphology of the ynthesized magnetic particles play a crucial role in ensuring the stability of magnetic fluids in a liquid medium. Figure 2 shows a TEM image of the Co**Fe$_2$O$_4$** ferrite-based magnetic fluid. From this image, it can be seen that the Co**Fe$_2$O$_4$** nanoparticles, which exhibit the main magnetic properties, are predominantly spherical in shape. The formation of aggregates of magnetic nanoparticles in magnetic fluids reduces the stability of the nanofluids. However, it was found from this TEM image that almost no nanoparticle aggregates had formed. Furthermore, using TEM imaging, the sizes of the Co**Fe$_2$O$_4$** ferrite particles in the magnetic fluid were obtained as a histogram form. The average diameter of the magnetic particles was found to be 9.3 nm. The stability of magnetic fluids based on magnetic particles of this small size is very high. The TEM image of the sample and the size histogram demonstrated that the magnetic fluid synthesis process was successfully carried out.

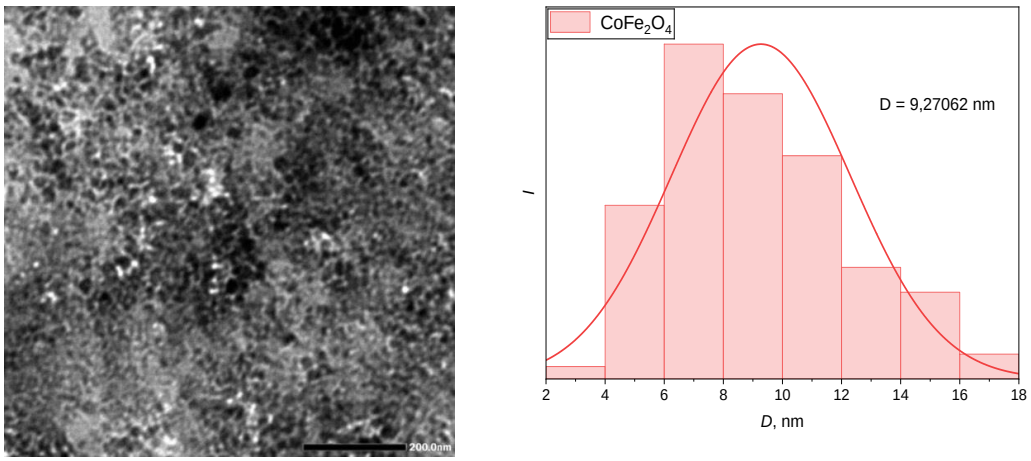


Figure 2. TEM images and size histograms of magnetic fluids based on $CoFe_2O_4$ nanoparticles.

The dependence of the relative magnetization of $CoFe_2O_4$ nanoparticle-based magnetic fluids on the external magnetic field was measured at room temperature using a vibrating magnetometer. The measurement result is presented in Figure 3. As shown in Figure 3, the sample's magnetization

increases with the magnetic field and reaches a saturation value. The samples' magnetic characteristics which saturation magnetization, remanence magnetization, and coercivity were determined using the magnetization hysteresis loop of the magnetic fluids. These values are presented in Table 1. According to the results, the coercivity of the sample is very low about 77 Oersteds indicating that the sample exhibits superparamagnetic behaviour. This, in turn, indicates that the size of the $CoFe_2O_4$ ferrite particles in the sample is much smaller than the single-domain size.

Table 1. Magnetisation results of magnetic fluids based on $CoFe_2O_4$ particles.

Magnit suyuqlik	***H*$_c$(Oe)**	***M*$_r$(emu/kg)**	***M*$_s$(emu/kg)**
$CoFe_2O_4$.	77	5.89	62,42

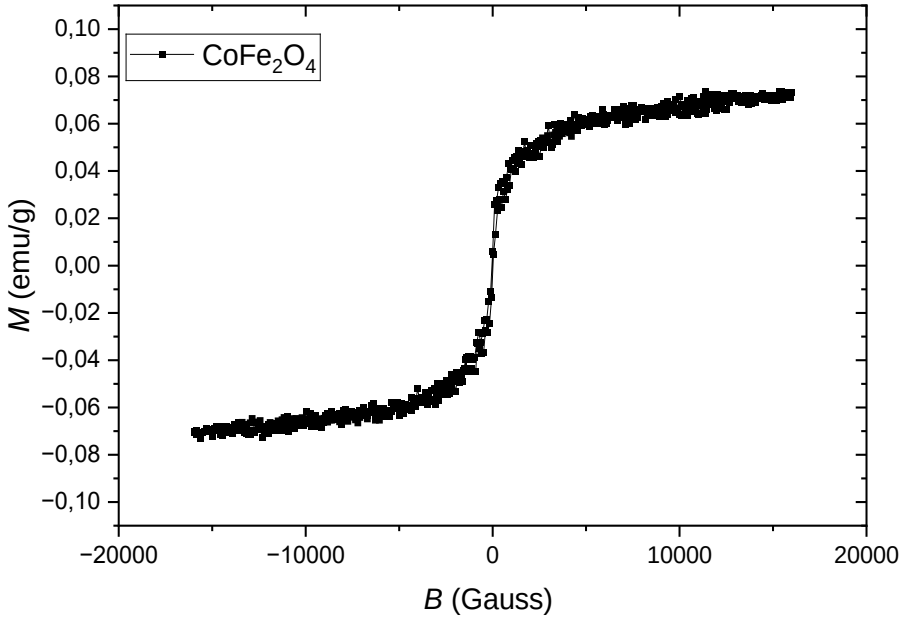


Figure 3. Magnetisation hysteresis of the $CoFe_2O_4$ based magnetic fluid.

The magnetic nanoparticles in magnetic fluids are distributed isotropically in volume. At room temperature, the magnetic moments of the particles are aligned in random directions, and the overall magnetisation is not formed. Under the influence of an external magnetic field, the magnetic moments of the magnetic particles align along the field and engaging dipol-dipol interaction with one another, form chain-like structures along the field (Figure 4). The formation of chain structures along the external magnetic field is one of the most fundamental magneto-optical properties of magnetically soft materials, such as ferrofluids.

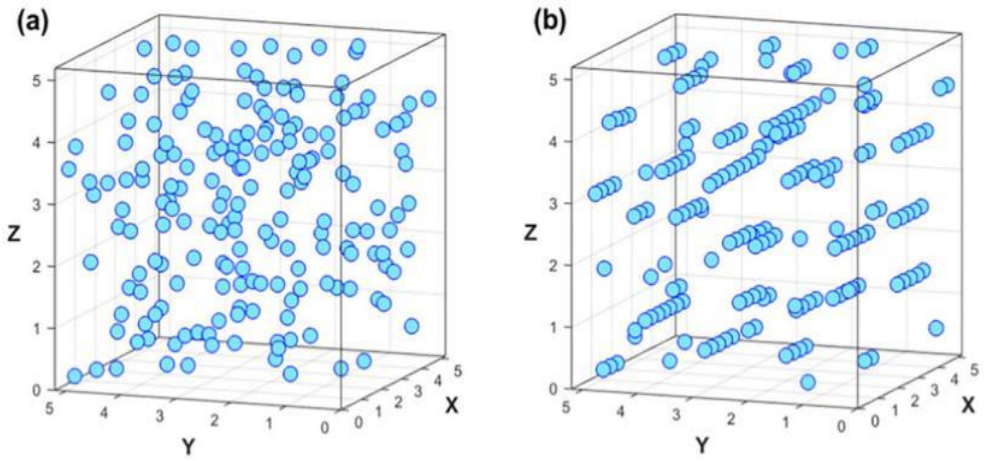
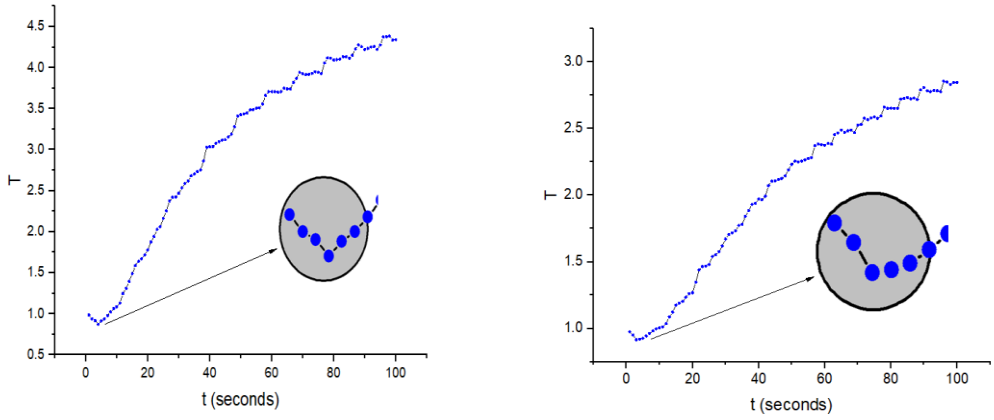


Figure 4. Disorganisation of ferrofluid particles under an external field (a), and the process of chain structure formation over time (b).

Figure 5 shows the time dependence of the magneto-optical transmission of a $CoFe_2O_4$ -based magnetic fluid. The sample was subjected to two different fields (800 T and 500 T) over a period of 100 seconds. Analysis of the experiments shows that under the influence of an external magnetic field the system's optical properties exhibit a nonlinear time dependence, with the process occurring in several stages. In the initial stage of the experiment, the light transmission decreases over a short period of time, about 0–10 seconds. This occurs because, as soon as the magnetic field is switched on, the magnetic nanoparticles orientate rapidly and, through interparticle dipol-dipol interactions, begin to form chain-like and cluster structures, leading to an increase in optical density in a specific region of the sample. As a result, light scattering in that regions cause the decreasing the intensity of light passing through the medium. Figure 5 illustrates the evolution of magnetic ferrofluid particles from an initially disordered state to the formation of chain-like structures under the application of an external magnetic field.



(5) (b)

Figure 5. (a) Time dependence of the light transmission value under the influence of an external field of 800T, (b) time dependence of the light transmission value under the influence of an external field of 500T.

Over the subsequent interval, the gradual increase in light transmission is associated with the stabilization of the structural configuration formed in the magnetic fluid. Chain-like structures align themselves along the direction of the magnetic field, restoring the medium's optical homogeneity to some extent, which leads to a reduction in light scattering and an increase in light transmission. In the final stage of the process, the rate of change of the transmission values slows down, and the system approaches an equilibrium state.

Furthermore, it was found that the samples' light transmission also changes depending on the value of the external magnetic field (Figure 5). At an external magnetic field of 800 mT, the sample's transmission was found to increase at a faster rate compared to a field of 500 mT. This, in turn, is explained by the stronger magnetization of the nanoparticles in high magnetic fields and their stronger interparticle dipole–dipole interactions. The slight fluctuations observed in the Figure5 are explained by the thermal motion of the magnetic nanoparticles and the instrumental uncertainties of the measurement system.

Conclution. $CoFe_2O_4$ nanoparticles were synthesized by a chemical co-precipitation method and stabilized in distilled water using oleate sodium molecules to prepare magnetic fluids. The TEM image of the obtained magnetic fluid sample showed that the $CoFe_2O_4$ particles in the fluid were spherical in shape, with an average diameter of approximately 10 nm. The magnetization hysteresis of the magnetic fluid was measured at room temperature, and it was determined that the sample exhibits superparamagnetism state. The magneto-optical transmission of the $CoFe_2O_4$ -based magnetic fluid was investigated as a function of the external magnetic field and time. Over time, the transmission initially decreased and then increased sharply. At high external magnetic field strengths, the light transmission in the ferrofluid samples was found to increase significantly, demonstrating that the intensity of the light passing through the sample can be controlled by the external magnetic field.

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