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МАГНИТНЫЕ НАНОЧАСТИЦЫ Fe_3O_4@C: СИНТЕЗ, МОРФОЛОГИЯ, МАГНИТНЫЕ СВОЙСТВА И ПРИМЕНЕНИЯ

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Аннотация *Работа посвящена исследованию магнитных наночастиц Fe_3O_4@C, синтезированных методом термического разложения с использованием трех различных маршрутов синтеза: (1) двухстадийный процесс, когда предварительно синтезированные наночастицы Fe_3O_4 покрываются углеродом, (2) наночастицы в одностадийном процессе получения покрываются углеродом, и (3) эти наночастицы ядро-оболочка покрывались дополнительной углеродной оболочкой. Изучены морфология и особенности магнитных и магнитооптических свойств полученных гибридных наночастиц. Исследованы адсорбционные свойства наночастиц по удалению катионных и анионных красителей из водных растворов.*

MAGNETIC NANOPARTICLES FE_3O_4@C: SYNTHESIS, MORPHOLOGY, MAGNETIC PROPERTIES AND APPLICATION

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Annotation. *The work is devoted to the study of the Fe_3O_4@C magnetic nanoparticles synthesized with the thermal decomposition method using three different synthesis routes: (1) two stage process when preliminary synthesized Fe_3O_4 nanoparticles were covered by carbon, (2) core-shell nanoparticles were prepared in the one stage process, and (3) these core-shell nanoparticles were covered with the additional carbon shell. The morphology and features of the magnetic and magneto-optical properties of the obtained hybrid nanoparticles were studied. The sorption properties of NPs for the removal of dyes have been studied.*

Keywords: *core-shell Fe_3O_4@C nanoparticles, adsorption, magnetic properties*

Magnetic nanoparticles (NPs) have been widely studied for a long time and are considered as very perspective materials for modern technologies. One of the advantages of magnetic NPs is associated with their ability to be easily extracted from the medium by applying magnetic field. In this regard, Fe_3O_4@C NPs are rather attractive to be used for the polluted water treatment since they combine the good adsorption properties of carbon, a developed and large specific surface area, and the magnetic properties of magnetite. Several authors carried out experiments on the pollutants removal from water with Fe_3O_4@C NPs [1]. They were used as sorbents of heavy metals (Cu, Ni, Co, and Cd) [2], poly-aromatic carbons [3], brominated flame retardants and pentachlorophenol [4], methylene blue (MB) and cresol red (CR) [5,6,7,8].

A number of synthesis methods leads to a large variety of the NPs properties. Therefore, the study of particles obtained by various methods, the determination of their properties and the search for applications remains an urgent problem and requires research in each case. The present work is devoted to the study of the morphology, magnetic and adsorption properties of Fe_3O_4@C NPs obtained by thermal decomposition method using several synthesis routs. The methylene blue (MB) was selected as a typical organic pollutant to test the ability of the Fe_3O_4@C composite for adsorptive removal of organic pollutant from water.

The Fe_3O_4 NPs (sample 1A) were synthesized with thermal decomposition of iron (III) acetyl-acetonate Fe in benzyl alcohol in an argon stream at 200 °C for 2 hours. After cooling the mixture, the nanoparticles were separated from the suspension by a magnetic field, then product was washed several times with ethanol by magnetic decantation and dried at 30 °C for 6 hours. To prepare nanocomposite Fe_3O_4@C (sample 1B), the obtained Fe_3O_4 NPs were mixed with glucose solution for 30 min and heated in a teflon autoclave at 200°C for 12 hours. After cooling, the

nanoparticles were separated by a magnet and washed several times with water and ethanol, and dried at 60 °C for 6 hours. The sample 2A was synthesized by a one-stage thermal decomposition of a mixture of iron (III) nitrate monohydrate, oleic acid (OA), and oleylamine (OLA). Oleic acid pyrolysis was used in our synthesis as a carbon source for coating iron oxides. The reaction took place in an argon stream at T ≤ 395 °C. To prepare sample 2B, the solution of powder 2A with glucose was placed in a Teflon autoclave at 200℃ for 12 hours.

The synthesized samples were examined by X-ray diffraction (XRD), transmission electron microscope (TEM), vibrating sample magnetometer (VSM), and magnetic circular dichroism spectroscopy (MCD). Experiments were carried out on the MB extraction with NPs from the water solution.

Figure 1 shows the NPs morphology transformation when coming from sample 1A to 2B. In the parent 1A sample, well-dispersed spherical NPs of about 10 nm in diameter are seen (Fig.1a), coatings them with carbon led to the formation of large carbon plates with NPs interspersed (Fig. 1c). In sample 2A, most of particles demonstrate spherical shape but have essentially larger diameter comparing to sample 1A. Alongside with these NPs, faceted and polygonal shaped NPs are observed (Fig. 1b). In sample 2B, the last one's become larger, their quantity arises strongly and spherical NPs can be noted in their background (Fig. 1d). Origin and composition of polygonal NPs are not clear yet.

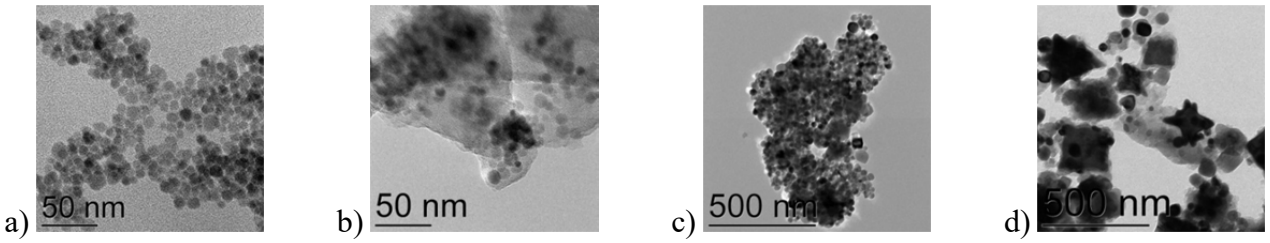

Fig. 1. TEM images of samples 1A (a), 1B (c), 2A (b), and 2B (d)

The magnetization curves are shown in Fig. 2a. The practical absence of hysteresis in the case of 1A and 1B samples evidences their superparamagnetic state at room temperature. Hysteresis is observed in samples 2A and 2B, at that the coercivity is noticeably larger in sample 2B. This behavior is consistent with the particle sizes in the samples seen in the TEM images. In all cases, the NPs magnetization remains rather large which is sufficient for their application.

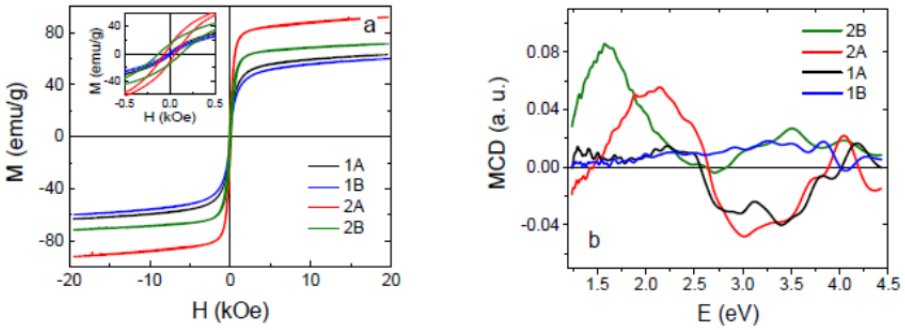

Fig. 2. Magnetization loops (a) and the MCD spectra at H = 13 kOe (b) of the samples measured at room temperature.

The MCD spectra (Fig. 2b) of the samples demonstrate strong changes at the transitions from one sample to another. Since the form of the MCD spectrum has a certain form characteristic of a certain phase, this tells us that the phase composition in each case is not pure; the NPs most likely contain a mixture of iron oxide phases. Only in 1A and 2A cases MCD spectra are similar to the spectrum of magnetite. MCD of sample 1A has a much lower value. This could be due to the very small size and superparamagnetic behavior of the NPs in this sample. The process of the carbon coating of already obtained nanoparticles, both in 1B and in 2B cases, leads to a significant change in the MCD spectrum which can be caused by a change in the phase composition.

The sorption properties of the particles were determined according to the standard procedure. The dye concentrations were determined by measuring at the maximum adsorption of MB at the light wave length 660 nm using a spectrophotometer. At any time, the amount of dye adsorbed onto the adsorbent (q_t) was calculated by the following equation:

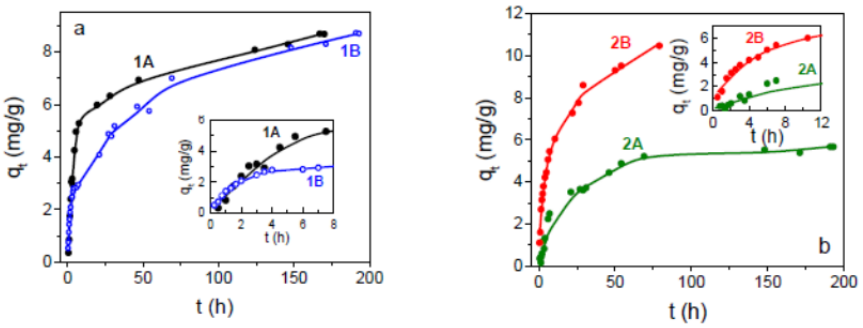

Fig. 3. The effect of contact time on the adsorption of MB for 1A, 1B samples (a) and for 2A, 2B samples (b). The inset shows a section of short adsorption times. Experimental conditions: C_0=30 (mg/l), m(NP)=3 (mg) in V=1.5 (ml).

$$q_t = \frac{(C_0 - C_t)V}{m},$$

here C_0 (mg/l) is the initial MB concentration, C_t (mg/l) is the dye concentration at any time t, V is the volume of the liquid and m (g) is the mass of the absorbent. The specific features of the adsorption of each sample are clearly seen in Fig. 3.

The description of the adsorption curves by kinetic models of the pseudo-first ($\ln(q_e - q_t) = lnq_e - k_1 t$) and pseudo-second ($t/q_t = 1/k_2 q_e^2 + t/q_e$) order showed closeness to the kinetic model of the pseudo-second order, and therefore the sorption process in our case can be controlled by chemisorption. Where q_e is the equilibrium sorption value, k_1, k_2 are the rate constants of the sorption of the reaction of the pseudo-first and pseudo-second orders, respectively. The determined correlation coefficients are equal 0.917 (1/h) and 0.995 (g/mg·h) for each case, respectively.

The dependences of the adsorption value on the initial concentration of the dye have one plateau, and they belong to type I adsorption isotherms, therefore, we can talk about monomolecular sorption. A quantitative description by the Langmuir and Freundlich equations showed that the adsorption of MB on the surface of the studied nanoparticles is well described by the Langmuir theory of monomolecular adsorption. Sample 2 has the highest absorption capacity.

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