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APPLICATION OF MAGNETIC NANOPARTICLES FOR WATER TREATMENT

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Abstract: In this study magnetic nanoparticles were fabricated and used for water treatment. Nanoparticles were prepared in two ways. The first one involved NiZn ferrite nanoparticles synthesized by co-precipitation of metal cations with sodium hydroxide at high temperature. The second one featured maghemite nanoparticles was prepared by salt-assisted solid-state reaction. Modification and functionalization of nanoparticles surface was investigated. Nanoparticles were characterized by scanning electron microscopy (SEM). Modified nanoparticles were added to the solution of desired concentration of methylene green. Adsorption ability was examined trough ultraviolet-visible spectroscopy (UV-VIS). For NiZn ferrite and also for maghemite nanoparticles results were positive. Both of complexes can be used for water treatment with 51% success for maghemite and 72% for NiZn ferrite nanoparticles.

Keywords: magnetic nanoparticles, water treatment, cyclodextrins, maghemite, absorption spectrophotometry.

Introduction

Nanotechnology is a science which describes phenomena in “nano” scale. “Nano” means 10^{-9} m. Nanomaterials have unique properties compared to classic materials. One of these properties is increased ratio of surface to volume. Another interesting example is growth of reactivity with a decrease in size. Mentioned properties are also applied to magnetic nanoparticles.

Magnetic nanoparticles are popular in different fields. For example in biotechnology, medicine (magnetic resonance), data storage, environmental protection and others. When we achieve properly small size (10-20 nm) through increasing ratio of surface to volume, some surface atoms may be coupled with their neighbors. This phenomenon causes ferromagnetism. Individual magnetic nanoparticles may be single domains and they may have superparamagnetic properties. We also know that single nanoparticles have a large constant magnetic moment. That’s why they behave like gigantic paramagnetic atoms with rapid response to applied magnetic field, residual remanence and coercivity. Materials which are characterized by large coercivity and remanence are called hard magnetic materials. On the other, hand soft magnetic materials means have low coercivity [1].

One of the goals of my work was synthesis of magnetic nanoparticles modified by cyclodextrin. The inspiration for me was A.Z.M. Badruddoza’s paper. Authors of this paper applied magnetic nanoparticles modified by β-Cycylodextrin (β-CD) to remove methylene blue from water.

β-Cyclodextrin is a compound of seven glucose mers in torus shape (Fig. 1a). The inner surface of β-CD have hydrophobic properties and the outer surface is hydrophilic. Van der Waals, hydrophobic interactions and hydrogen bonds are responsible for cyclodextrin-organic compounds interaction. These types of interactions are called guest-host interactions. This feature is used in industry and technology for water treatment. Grafting carboxyl groups onto CD increases their adsorption properties [2].

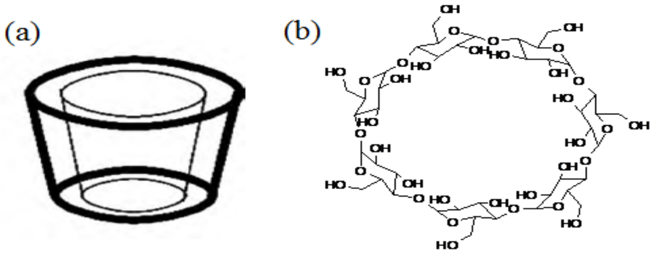

Fig.1. Toroid shape (a) and chemical structure (b) of β-CD.

Materials and methods

In this work chemical reagents were purchased from producers mentioned in Tab.1 below.

Following chemical equipment was used: Bandelin Sonorex ultrasonic cleaner, UV-vis Lambda 10 spectrophotometer, FEI Quanta FEG 250scanning electron microscope, High Speed Brushless Centrifuge MPW 250centrifuge, POLL Lab Q-Flow fume hood, Heidolph MR-Hei-Standard magnetic stirrer and Kern EG 420-3 NM weighing scale.

Tab.1. A list of used chemical reagents.

Producer's name	Chemical reagent
POCH	$FeCl_3$, KCl, KOH, isopropanol, ammonia, xylene, HCl, DMF, acetone, HNO_a
Sigma - Aldrich	$Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $FeCl_2{\cdot}4H_2O$, APTES, β-CD, toluenesulfonyl chloride
Fluka	Tetraethyl orthosilicate, NaOH, methylene green

Preparation of magnetic nanoparticles

Nickel-zinc nanoparticles ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) were prepared by method described in P. Majewski's master thesis [3]. Each of the ingredients was used in 20 times smaller amount. The precursor solution was received through melting of $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ in millipore water. Next step included preparation of aqueous solution NaOH and HNO_3. To the three-nacked flask acidulated precursor solution (2 mol/dm^3 HNO_3) and distilled water was poured. Whole mixture was heated to 95˚C while stirring. In separate vessel NaOH solution was also heated to 95˚C. Obtained product was then purified through 3 times rinsing with distilled water, ultrasonic bath and decanting. After this centrifuging and drying (3 minutes, 13 000 rpm) were carried. Powder was achieved in this method (Fig. 2a). This powder was characterized by scanning electron microscopy (Fig. 2b).

Maghemite nanoparticles were also prepared through method described in J. Lu's paper [4]. Weighted portion of $FeCl_3$, KCl and $FeCl_2{\cdot}4H_2O$ were pounded in a mortar to obtain yellow paste. In next step KOH was added and pounded for 15 minutes. After change of the color (from yellow to brown) this paste was purified and centrifuged. Dried particles (Fig. 3a) were characterized by SEM (Fig. 3b).

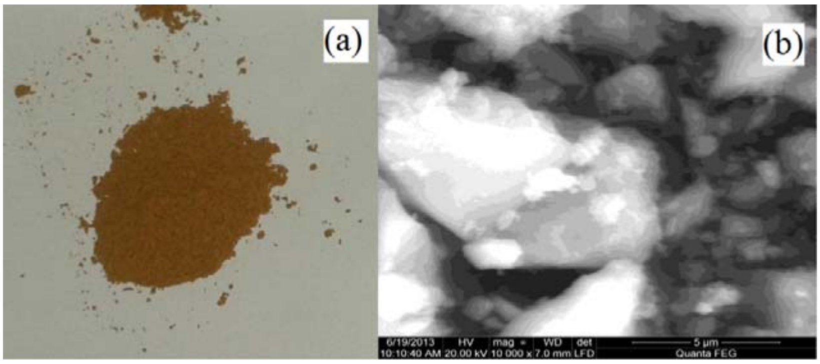

Fig. 2. NiZn ferrite before silica gel coating as a powder (a) and on a SEM picture (b).

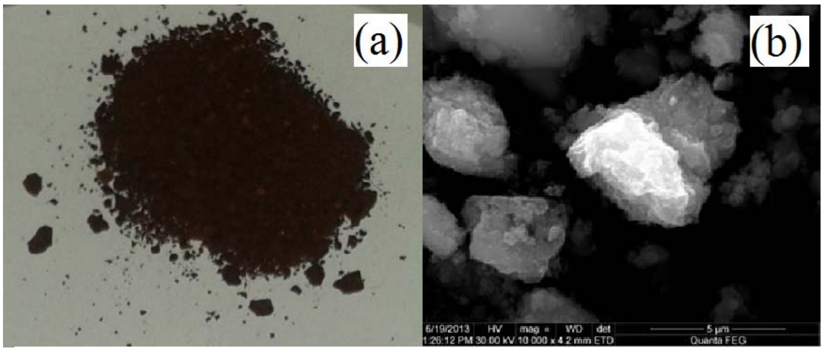

Fig. 3. Maghemite before silica gel coating as a powder (a) and on a SEM picture (b).

Modification and functionalization of magnetic nanoparticles

Next steps (Fig. 4) were the same for both of nanoparticles. Before modification nanoparticles should be prepared. Magnetic nanoparticles were covered with silica gel. The objective was to protect particles from oxidation and agglomeration.

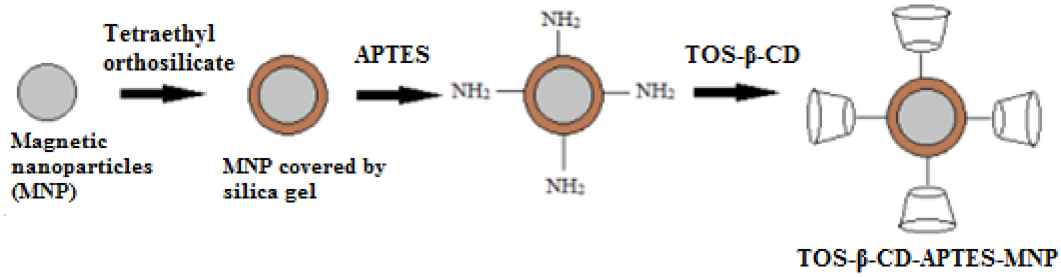

Fig. 4. Modification schema.

Modification process was based on Younan Xia's article [5]. Distilled water was added to nanoparticles and then a 10-minute ultrasonic bath was carried. After that isopropanol, ammonia and tetraethyl orthosilicate was added. This mixture was then sonicated and centrifuged. Dried particles were characterized by SEM (Fig. 5, 6).

In the following part functionalization of nanoparticles' surface was obtained with (3-aminopropyl)triethoxysilane (APTES). Meanwhile, basing on R.C. Petter's paper [6] 6-O-monotosyl-β-CD was prepared. 0.4 M NaOH solution was added to β-CD. Then under continuous stirring toluenesulfonyl chloride (TOS) was added. This solution was left on magnetic stirrer for 3 h in 0˚C. Product was filtered, neutralized with 1 M HCl and dried under reduced pressure. Obtained powder of TOS-β-CD was used to modify nanoparticles. After adding TOS-β-CD ingredients were drenched with dimethylformamide (DMF) and sonicated for 7 h in 60˚C. The outcome was centrifuged, washed and dried.

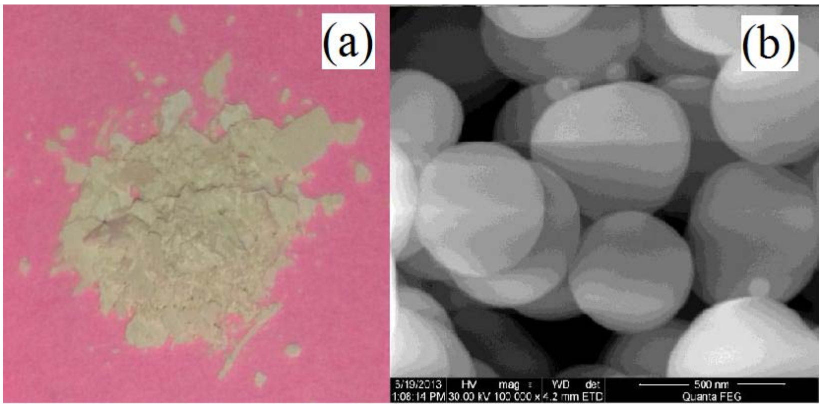

Fig. 5. NiZn ferrite after silica gel coating as a powder (a) and on a SEM picture (b).

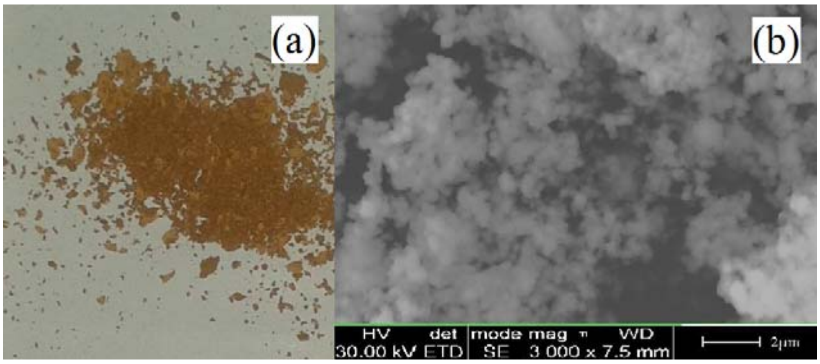

Fig. 6. Maghemite after silica gel coating as a powder (a) and on a SEM picture (b).

Water treatment

The final stage was application of modified magnetic nanoparticles for pollutants removal. This part was based on A.Z.M. Badruddoza's article [2]. In this work methylene green was used as organic pollutant. Effectiveness of dye removal was confirmed with absorption spectroscopy method. Methylene green in aqueous solution has his absorption maximum at 611 nm (Fig. 7).

Solutions of methylene green were prepared in various concentrations: 10^{-7}-$5\cdot10^{-4}$ M. Absorption spectra were recorded for mentioned solutions in range 200-800 nm. Based on the results a graph of absorbance versus concentration was made. The calibration curve (Fig. 8) was drawn. A concentration that was used later to remove dye from water was selected. Concentration of methylene green and number of adsorbed dye's mols after 1 h and 24 h after adding modified nanoparticles was calculated. Solution of methylene green with magnetic modified nanoparticles was poured to quartz cuvette and then placed on neodymium magnet until the deposition of nanoparticles on the bottom of the vessel. To demonstrate that adsorption doesn't occur without CD, a measure of absorbance for solution with dye and nanoparticles without CD was investigated.

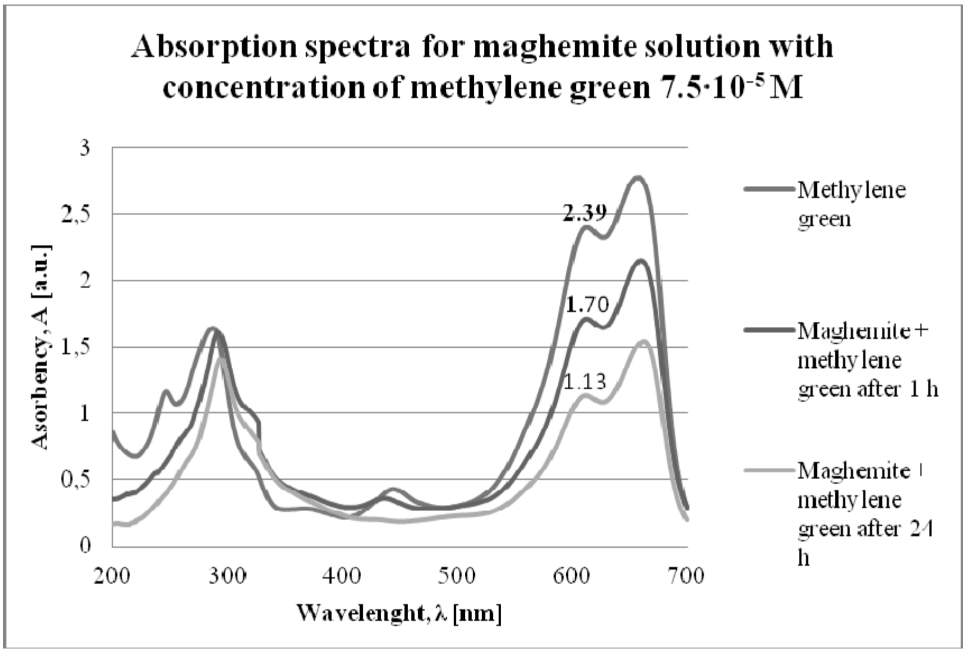

Fig. 7. Absorption spectra for maghemite nanoparticles.

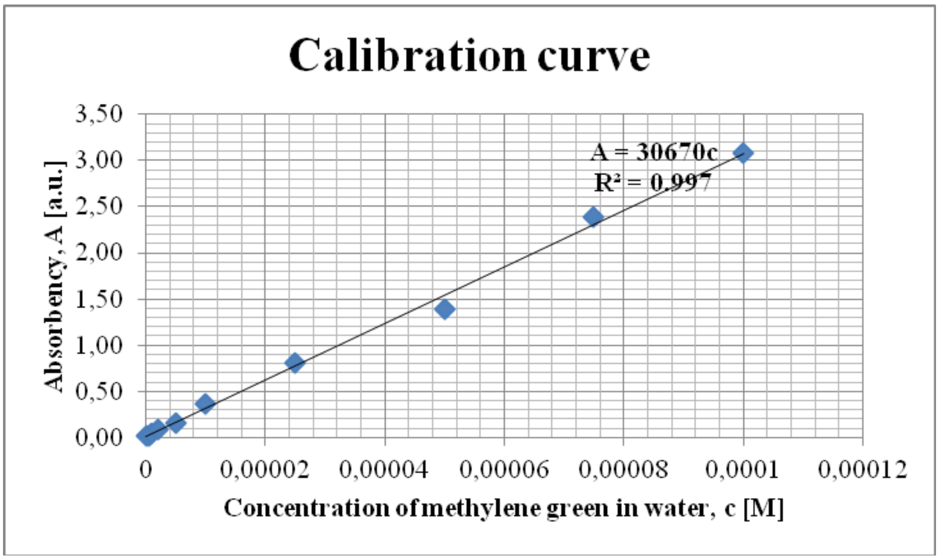

Fig. 8. Calibration curve made to choose methylene green concentration for further research.

Results

Maghemite and NiZn ferrite nanoparticles were fabricated. The resulting powder before (Fig. 2, 3) and after being coated with silica gel can be seen at the Fig. 5 and 6.

Based on resulting measurements of absorbency for various concentrations of methylene green in water, a graph of absorbency versus concentration was made. The calibration curve (Fig. 8) was drawn.

Exemplary measurement of absorbency for solution with maghemite is shown below (Fig.8). Concentration of methylene green in water is $7.5\cdot10^{-5}$ M. Presented results were obtained after 1 h and 24 h.

Dye concentration after adding modified nanoparticles was calculated. Absorption value was inserted to the equation from Fig. 8. The results are presented below (Tab. 2).

Tab.2. Dye concentration in water after adding modified nanoparticles. Results are based on the decrease in absorbency.

Nanoparticles	Dye concentration after 1 h	Difference of dye concentration between outcome and observed solution	Dye concentration after 24 h	Difference of dye concentration between outcome and observed solution
$Ni_{0.5}Zn_{0.5}Fe_2O_4$	$3.98\cdot10^{-5}$ M	$3.52\cdot10^{-5}$ M	$2.12\cdot10^{-5}$ M	$5.38\cdot10^{-5}$ M
Maghemite	$5.54\cdot10^{-5}$ M	$1.96\cdot10^{-5}$ M	$3.68\cdot10^{-5}$ M	$3.82\cdot10^{-5}$ M

The amount of adsorbed nanoparticles (mg) is calculated below.

Molar mass of methylene green: 364.85 g/mol.

Mass of NiZn ferrite nanoparticles added to 3 ml solution of methylene green: 38 mg.

Mass of maghemite nanoparticles added to 3 ml solution of methylene green: 40 mg.

Based on the difference in concentration of the dye (Tab.2), the amount of adsorbed dye's mols after 24 h was calculated. We can see that 38 mg of NiZn ferrite nanoparticles adsorbed $16.14\cdot10^{-8}$ mol. This means that 1 g of these nanoparticles adsorbed $0.42\cdot10^{-5}$ mol of dye and 1,5 mg of dye was adsorbed onto 1 g of nanoparticles.

In case of maghemite nanoparticles 40 mg of nanoparticles adsorbed $11.46\cdot10^{-8}$ mol. This means that 1 g of these nanoparticles adsorbed $0.29\cdot10^{-5}$ mol of dye and 1 mg of dye was adsorbed onto 1 g of nanoparticles.

Discussion and conclusions

After first step of synthesis a brown powder of nanoparticles (NiZn ferrite and maghemite) was produced (Fig. 2a, 3a). In both of cases obtained particles had crystal-like shape (Fig. 2b, 3b) with different diameters. The largest had 50 µm in diameter. After silica gel coating agglomeration effect disappeared, they had regular, spherical shape and similar diameters up to 500 nm. (Fig. 5b, 6b). Most likely the loss of smaller nanoparticles was caused during washing process. Further surface modification was successful. The evidence of that was increased mass of nanoparticles. Based on calibration curve (Fig. 8), the concentration of methylene green was selected as $7.5\cdot10^{-5}$ M.

To demonstrate that there is no adsorption without cyclodextrins, absorbtion spectra of solution methylene green with nanoparticles without CD were investigated. The results showed that there were no changes before and after measurement. Absorbency did not change after 24 h. It was 2,39 a.u. before and after adding nano-particles. Based on Tab.1 we can see that after 1 h, the concentration of methylene green decreased to about half of its initial value (~47%) for NiZn ferrite nanoparticles. After 24 h it decreased 4 times (~71%). For maghemite nanoparticles concentration of methylene green after 1 h decreased about 26% and after 24 h about 51%. Calculations show 1.5 mg of dye was adsorbed onto 1 g of NiZn ferrite nanoparticles and 1 mg of dye was adsorbed onto 1 g of maghemite nanoparticles. For methylene blue [2] results were significantly better: 100 mg of dye were adsorbed onto 1 g of magnetic nanoparticles. This difference is caused by the loss of smaller nanoparticles during washing process. Average surface area of adsorbent was reduced. The lower is specific surface area, the less CD is incorporated to nanoparticles surface per unit. There were less places responsible for dye complexing. Furthermore chemical structure of methylene makes it less complex than methylene blue because of nitrille group.

Formation of a complex was also affected by the initial concentration of a dye. In this work low concentration (similar to that in the wastewater) was investigated. Concentration of individual compounds in wastewater after treatment is too low to be measured. This is the reason why this method could be a solution to the problem of measuring very low concentrations of water contamination after cleaning.

It should be noted that application of magnetic nanoparticles covered by silica without CD didn't lead to dye removal. In this process there is no adsorption onto porous material (outer surface of silica). Adsorption occurs in the cavity of CD. It is easy to see that NiZn ferrite nanoparticles are a better adsorbent than maghemite.

Synthesis and modification of magnetic nanoparticles were investigated. Morphological properties were carried with scanning electron microscope technique. The adsorption of methylene green with and without CD after 1 h and 24 h was studied. Presented application of magnetic nanoparticles for contaminations removal was effective. NiZn ferrite and maghemite nanoparticles decreased concentration of dye in water. NiZn ferrite nanoparticles were a better adsorbent. Concentration of methylene green decreased about 72% after 24 h. Obtained results are interesting for further research.

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