Preparation of Magnetic Sorbent with Surface Modified by C$_{18}$ for Removal of Selected Organic Pollutants from Aqueous Samples

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Abstract. Magnetic sorbents have great potential in environmental applications due to their simple synthesis and separation in magnetic field, usability in heterogeneous systems and low toxicity. Possible syntheses, surface modifications and characteristics were described by Li et al 2013. This type of solid-phase extraction is being successfully used in various fields as health care, microbiology, biotechnologies or sample preconcentration in analytical chemistry. In this preliminary study we report on the preparation and application of magnetically separable sorbent with surface modified by C$_{18}$ alkyl chain for purification of water contaminated by environmentally hazardous organic compounds. Magnetic cores were co-precipitated from Fe$^{2+}$ and Fe$^{3+}$ chlorides in alkalic aqueous solution. Surface of synthetized Fe$_3$O$_4$ was modified with SiO$_2$ by tetraethylorthosilicate to assure physico-chemical stability. Furthermore, Fe$_3$O$_4$/SiO$_2$ complex has been treated by C$_{18}$ functional group, which provides good affinity towards hydrophobic substances in water. Efficiency of sorption under various conditions has been examined on benzene, toluene, ethylbenzene and xylenes (BTEX), compounds found in petroleum products which contaminate air, soil and groundwater near of store tanks. Sorption kinetics was followed by gas chromatography with mass spectrometry. The preliminary sorption kinetics data and efficiency of BTEX removal point at the possible application of prepared magnetic sorbent for BTEX removal, especially for ethylbenzene and xylenes.

1. Introduction

Magnetically separable sorbents offer certain advantages in environmental applications and designing new environmentally friendly technologies due to their simple synthesis and separation by means of magnetic field [1, 2]. Magnetite with different deposits and coatings on its surface was used for extraction of heavy metals and radionuclides[3, 4], removal of organic dyes [5], isolation of pathogenic microorganisms [6] etc. It can also be used as catalysts, Gawunde et al. prepared magnetic sorbent for applications as catalyst in multicomponent reactions under benign conditions [7]. Recently, Janoš et al. [8] reported on magnetically separable reactive sorbent based on the CeO$_2$/Fe$_3$O$_3$ composite for rapid degradation of the organophosphate pesticide parathion methyl and nerve agents such as soman and VX.
Commonly used principles of interaction of modified magnetite with target analytes are adsorption, ion-exchange, ligand affinity or interaction of antigen and antibody. Favourable active deposits and coatings are based on silica, manganese oxide, alkyl chains, or polymers. The role of deposit and coating is to protect Fe₃O₄ cores, provide higher surface area and biocompatibility. Another strategy to reach magnetic separation is dispersion in sorbent matrix [9]. Separation device may consist of strong permanent magnets or electromagnets, which provides simpler handling. The most effective and continuous method even for the smallest fraction is separation in HGMS (High Gradient Magnetic Field). For large volumes of treated water are suitable drum separators [10].

In this paper the BTEX (benzene, toluene, ethylbenzene and xylenes) compounds were selected for the preliminary study of sorption ability of prepared magnetic sorbent modified with C₁₈. This group of volatile organic compounds can be found in petroleum hydrocarbons, such as gasoline, and other common environmental contaminants. They constitute one of the most common and serious threats to groundwater reservoirs and indoor climate deriving from contaminated sites. This is mainly due to the potential effects of benzene, which is considered a strong carcinogen. Moreover, all BTEX are highly mobile in the soil and groundwater environment.

The main aim of this work was to prepare the magnetic sorbents with surface modified by SiO₂ and C₁₈ by described procedure and examine their sorption ability by preliminary experiments with BTEX in model aqueous samples.

2. Experimental work
The magnetic cores have been obtained by co-precipitation of 0.2 M iron(III) chloride hexahydrate (Lachema) and 0.1 M of iron(II) tetrahydrate (VWR chemicals) in solution of deionized water and NaOH (Lach-Ner). Synthesis ran for two hours under pH 10.0 – 10.5, nitrogen atmosphere and continuous mixing (300 rpm). These conditions assure the formation of ultra-fine grained particles of precipitated Fe₃O₄. Two types of surface modification have been performed – deposition of SiO₂ and binding of C₁₈ chain. The deposition of SiO₂ was carried out using the Stöber process [11] based on sol-gel interaction. Tetraethyl orthosilicate (Sigma-Aldrich) was hydrolyzed and condensed on the surface of Fe₃O₄ in solution of deionized water, ethanol and ammonium hydroxide (Lach-Ner) as a catalyst. The synthesis ran under inert atmosphere to reduce oxidation effects. As a precursor of C₁₈ chains served chlordimethyl-n-octadecylsilane(Alfa Aesar) dissolved in toluene with the presence of triethylamine (Sigma-Aldrich) and external heating. This mixture was refluxed for five hours at 140 °C, then decanted and washed with isopropanol. Expected particle size of final product using these methods is about 50 nm, which assures high surface area. Synthesized sorbents were dried and stored in gas-tight vials on a dark place.

The sorption ability of prepared magnetic sorbents was tested on 50 mg/l solution of BTEX in deionized water. Various amounts of both sorbent types was applied (0, 50, 500 mg) to test the sorption efficiency. After 96 minutes of reaction time, the suspension was decanted by magnetic field using magnetic rod purchased by Neomag. The small portion of aqueous decantate (1 ml) was transferred into 2 ml vial followed by addition of 400μl of dichloromethane. The vial was closed, shaken and analyzed with gas chromatography and mass spectrometry (GC 3800 MS 4000, Varian). The flow of carrier gas (He) in Agilent HP-88 column was set to 1 ml/min, temperature of injector to 240 °C. Thermal regime in column oven was following: 30°C, held 1 minute, gradient 5 °C/min up to 70 °C and 20 °C/min until 210°C, held 1 minute. All degradation experiments were conducted at the laboratory temperature of 295.15 K in an air conditioned box. In each series of measurements, blank experiments with the sorbent and solvents without the presence of BTEX were performed.
3. Results and discussions
The obtained results of sorption ability of prepared Fe$_3$O$_4$.magnetic sorbents with the surface modified only by SiO$_2$(Fe$_3$O$_4$/SiO$_2$ ) and C$_{18}$(Fe$_3$O$_4$/SiO$_2$–C$_{18}$) towards BTEX in aqueous samples for different amounts of sorbents (0 mg, 50 mg and 500 mg) are presented on figures 1 and 2.

![Figure 1](image1.png)

**Figure 1.** Effect of Fe$_3$O$_4$/SiO$_2$ magnetic sorbent on BTEX concentration in aqueous sample

![Figure 2](image2.png)

**Figure 2.** Decrease of BTEX concentration after extraction with Fe$_3$O$_4$/SiO$_2$–C$_{18}$ magnetic sorbent

It is distinct from the comparison of both figures that Fe$_3$O$_4$.magnetic sorbent with the surface modified only by SiO$_2$ does not exhibit significant sorption ability towards BTEX even after addition...
of higher amount (500 mg) of the sorbent. On the contrary the Fe₃O₄ magnetic sorbent modified by SiO₂ and C₁₈ shows remarkable sorption ability for all BTEX. The best sorption ability was observed for xylenes and ethylbenzene (nearly 100%), followed by toluene (70-80 %) and benzene (only 20-30 %). The relatively low sorption of benzene on C₁₈ in comparison to other BTEX can be explained by the highest solubility of benzene in water from all BTEX. Thus, there is a space for further research towards improvement of benzene extraction on C₁₈ from aqueous samples for example by salting out effect, moderate sample heating etc. The detailed study of sorption kinetics is also in progress.

4. Conclusions
Based on obtained results it is possible to state that the applied chemical way of surface modification of Fe₃O₄ has no effect on the magnetic properties of both prepared sorbents Fe₃O₄/SiO₂ Fe₃O₄/SiO₂–C₁₈. Both sorbents were easily separated from suspension by means of magnetic rod. Furthermore, it was shown that the surface of Fe₃O₄ magnetic sorbent modified by SiO₂ does not contribute significantly to the sorption of BTEX from aqueous samples. On the contrary the Fe₃O₄ magnetic sorbent modified by SiO₂ and C₁₈ exhibits significant sorption ability towards all BTEX ranging from 100 % for xylenes and ethylbenzene, 70-80 % for toluene and 20-30 % for benzene in dependence on their solubility in water.

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