TRANSFORMATIONS OF THE POROSITY PROFILES IN MAGNETITE-BENTONITE HYBRIDS

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The subject case is analyzed within the research devoted to the synthesis of the hybrid adsorbents. The hybrid nature implies the combination of eco-friendly and cheap clay (bentonite, BNT) with a magnetic component (magnetite, Fe_3O_4). These binary composites at gradually varied bentonite/magnetite ratio are intended for further modification to get highly enhanced adsorbents of oily products. Hence, specific surface area and textural properties (porosity, pores size distribution) of the basic hybrids are the very key properties which affect the effectiveness of the ready adsorbents and the rate of adsorption processes themselves. As bentonite acts as an adsorbent, magnetite phase is responsible for an immediate removal of the adsorbent from the treated media. Hence, the synthesis of the corresponding hybrid sets on the optimal junction of two individual phases.

The hybrid samples were synthesized at two stages: first, bentonite clay was pre-treated with HCl (under reflux within 24 hours, washed repeatedly with distilled water to pH 5.5-6), dried (100 ^oC), sieved and dried under vacuum at 60 ^oC. The processed BNT was labelled as HCl-BNT. Thereupon, Fe_3O_4 was deposited onto HCl-BNT via precipitation of $FeCl_3/FeSO_4$ salts in the presence of $NH_3 \cdot H_2O$ with certain modifications (heating, filtration, washing and drying) of the protocol originally published in [1]. The Fe_3O_4/HCl-BNT (w/w) ratios in the hybrid samples were set at 0.25:1, 1:1, 2:1 and 3:1 and the resulting samples were labelled respectively: Fe_HCl-BNT(0.25:1); Fe_HCl-BNT(1:1); Fe_HCl-BNT(2:1); Fe_HCl-BNT(3:1). Additionally, pure Fe_3O_4 was synthesized according the fore-mentioned procedure.

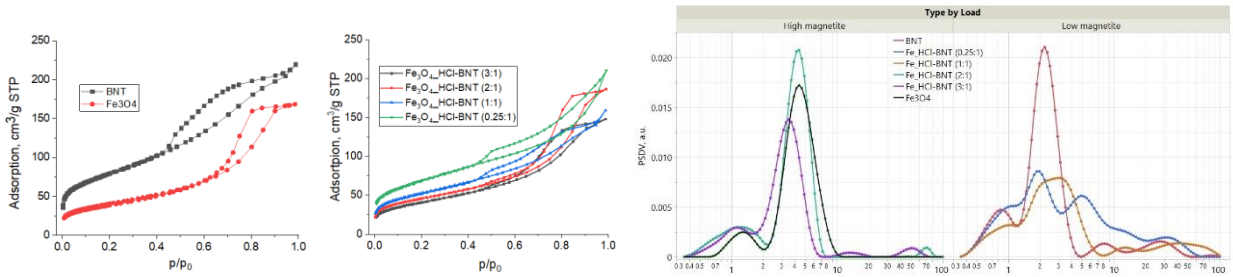
Within the scope of the present research Fe_3O_4, BNT and the Fe_3O_4/HCl-BNT hybrids were analyzed by means of the low-temperature nitrogen adsorption-desorption (77.4 K) using a NOVA 1200e analyzer (Quantachrome Instruments) to obtain the information about their textural properties. The porosity (total pore volume V_p) was calculated from the maximal adsorption, specific surface area (S_{BET}) was derived from the standard BET method within the $p/p_o = 0.05 – 0.35$ range. The pore size distribution was calculated using modified Nguyen-Do method for the models of slit pores (HCl-BNT) and for combinations of cylinders and slits in the case of the hybrid materials [2,3].

Morphology and stoichiometry of Fe_3O_4 was established with the help of SEM (Nova 600 Nanolab, FEI) equipped with an EDX accessory. The concentration of Fe was calculated from the FeL signal.

The BET curves at low loadings of magnetite - the samples Fe_HCl-BNT(0.25:1); Fe_HCl-BNT(1:1) - are comparable by their shape with BNT, i.e. their hysteresis curves speak for porosity similar to BNT (Fig.1a). With increased concentration of Fe_3O_4, the curves maintained hysteresis at weaker adsorption of nitrogen. The hysteresis loops changed gradually to the typical shape of Fe_3O_4 (Fig.1b). Such a curve for magnetite, Fe_HCl-BNT(2:1) or Fe_HCl-BNT(3:1), typical for mesoporous materials, was also reported elsewhere [4–6]. Hence, the synthesized hybrids must be regarded as materials with mixed porosities comprising pores size distributions from both materials and strongly depending on the composition.

The calculations for the pores size distribution revealed identical profiles among pure magnetite and the hybrids at the Fe_3O_4/HCl-BNT ratios of 2:1 and 3:1 (Fig.1c) with the main mode at R = 3-4 nm. The comparable distribution curve was also shown and discussed in [1]. Another two binary composites with

lowered concentration of magnetite demonstrated the principle modes at lower pores radii. Pure bentonite, BNT also contains micropores (R < 1 nm), represented by slit-shaped pores.



(a) (b) (c)

Fig.1. The BET curves of Fe_3O_4 and BNT – *(a)*, the Fe_3O_4/HCl-BNT hybrids - *(b)*, and the pores size distribution of all samples *(c)*

Thus, if the bentonite sample has slits, magnetite's pores are cylindrical. The dominating mesoporous nature is clearly reflected in Fe_HCl-BNT(2:1) and Fe_HCl-BNT(3:1) – more than 85% of the total pore volume (Fig.2). The specific surface area (S_{BET}) proportionally to the monolayer capacity (C_m) decreases with the augmentation of the Fe_3O_4 load also with the increase of the average pore radius. The BNT and Fe_HCl-BNT(0.25:1) feature in higher S_{BET} and the total pore volume.

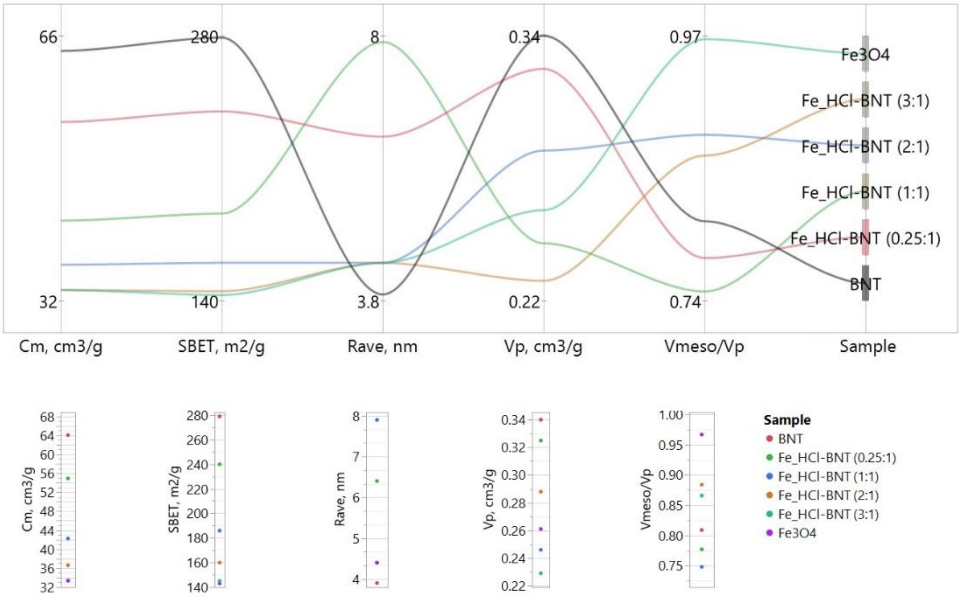


Fig. 2. The parallel plot of the summary for the textural properties calculated from the BET measurements.

Fe_3O_4 is characterized by high specific surface area (143 m^2/g), almost equal to the hybrid Fe_HCl-BNT(3:1) - 145 m^2/g. Thus, S_{BET} of bentonite decreased twice with transition to pure magnetite.

The SEM image evidenced porous nature of pure magnetite corroborating the results of BET measurements (Fig.3). The surface of the magnetite is not flat, it roughness could form during the room temperature nucleation process, which is observed in the hybrid samples at higher percentage of magnetite. The stoichiometry of Fe_3O_4 is proven from the EDX – ca. 30% of oxygen and ca. 70% of iron.

The proposed method of synthesis is promising for development of mesoporous adsorbents based on their mixed porosity controlled by the concentrations of components. The materials are projected to be

exposed to the surface modification together with thorough studies in magnetic susceptibility and ability to adsorb model contaminants.

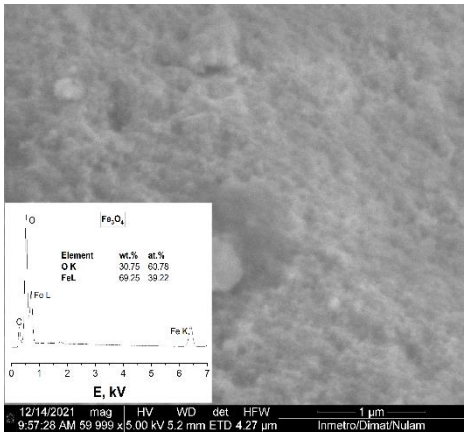


Fig.3. The SEM image of pure porous Fe_3O_4 with its elemental composition from EDX (inset).

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References:

[1] I. V Pylypchuk, D. Kołodyńska, M. Kozioł, P.P. Gorbyk, Gd-DTPA Adsorption on Chitosan/Magnetite Nanocomposites, Nanoscale Res. Lett. 11 (2016) 168. https://doi.org/10.1186/s11671-016-1363-3.

[2] V.M. Gun'ko, Composite materials: Textural characteristics, Appl. Surf. Sci. 307 (2014) 444–454. https://doi.org/https://doi.org/10.1016/j.apsusc.2014.04.055.

[3] V.M. Gun'ko, D.D. Do, Characterisation of pore structure of carbon adsorbents using regularisation procedure, Colloids Surfaces A Physicochem. Eng. Asp. 193 (2001) 71–83. https://doi.org/https://doi.org/10.1016/S0927-7757(01)00685-9.

[4] S. Lakshminarayanan, M.F. Shereen, K.L. Niraimathi, P. Brindha, A. Arumugam, One-pot green synthesis of iron oxide nanoparticles from Bauhinia tomentosa: Characterization and application towards synthesis of 1, 3 diolein, Sci. Rep. 11 (2021) 8643. https://doi.org/10.1038/s41598-021-87960-y.

[5] T. Zhao, R. Chen, J. Wang, A Mild Method for Preparation of Highly Selective Magnetic Biochar Microspheres., Int. J. Mol. Sci. 21 (2020). https://doi.org/10.3390/ijms21113752.

[6] N. Manikandan, B. Lakshmi, S. Shivakumara, Preparation of self-assembled porous flower-like nanostructured magnetite (Fe3O4) electrode material for supercapacitor application, J. Solid State Electrochem. 26 (2022). https://doi.org/10.1007/s10008-021-05097-4.