Conducting polymer composite aerogel with magnetic properties for organic dye removal

Conducting polymer composite aerogel with magnetic properties for organic dye removal

Patrycja Bober[a,*] Islam M. Minisy[a], Udit Acharya[a], Jiří Pfleger[a], Vladimir Babayan[b], Natalia Kazantseva[b], Jiří Hodan[a], Jaroslav Stejskal[a]

[a] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic*

[b] *Centre of Polymer Systems, Tomas Bata University in Zlin, 760 01 Zlin, Czech Republic*

** Corresponding author. E-mail address: bober@imc.cas.cz (P. Bober).*

ABSTRACT

Multifunctional conducting polyaniline/hexaferrite aerogels supported by poly(vinyl alcohol) have been prepared by simple one-step procedure. The incorporation of magnetic particles into aerogel matrix was successfully proven with scanning electron microscopy and by examination of magnetic properties. Such novel hybrid aerogels showed better resistance against elastic deformation when stress is applied, increased conductivity compared to neat polyaniline/poly(vinyl alcohol) cryogels, and also enhanced coercive force compared with neat hexaferrite due to increased effective magnetic anisotropy by magnetostriction. Moreover, the efficient adsorption of Reactive Black 5 dye by aerogel has been illustrated. Therefore, this work offers new type of macroporous dye adsorbents which can be efficiently separated from the aqueous medium and thus used for wastewater treatment.

Keywords: Polyaniline**,** Aerogel**,** Magnetic properties, Composites, Conductivity, Dye removal

1. Introduction

Electric and magnetic stimuli-responsive systems have attracted considerable attention during recent years due to a large array of applications including biosensors **[1,2]**, magnetic-resonance-imaging contrast agents **[3]**, supercapacitors **[4,5]**, fuel cells **[6,7]**, radio- and microwave absorbers **[8]** and electromagnetic-interference shielding materials **[9-11]**. Such materials contain, e.g., magnetic particles (different types of ferrites, iron oxides, carbonyl iron, etc.) incorporated in conducting polymer matrix **[12-20]**. Besides, hybrid composites based on conducting polymers and magnetic particles can be employed in various water-treatment methods for the capture, transfer, and removal of organic dyes and heavymetal ions from wastewater **[21-27]**. It is established, that the adsorbent capacity depends on its specific surface area and chemical nature of surface, as well as on adsorbent dosage, contact time, pollutant concentration, etc. The main advantage of magnetic adsorbents is that they can be rapidly and easily separated from water using a magnetic field.

Nowadays, with increased demand of textile products in human daily life, the reuse of wastewater containing dyes or heavy-metal ions in industry has become a worldwide environmental issue. Dyes and heavy-metals residues in wastewater are usually toxic, carcinogenic, mutagenic and inhibit the growth of aquatic biota. There are several treatment methods of their removal, like chemical oxidation, photocatalytic decomposition, filtration or adsorption. The preparation of new adsorbent materials with good selectivity, chemical and thermal stability, which could be easily and effectively separated using a low-cost technology, is the biggest challenge.

Conducting polymers, such as polyaniline or polypyrrole, have recently been investigated as materials for dye removal **[28,29]** by adsorption or photocatalytic decompostion. However, due to the poor processability and poor mechanical properties, their practical use is still limited. To overcome this problem, a new class of conducting composite materials represented by macroporous polyaniline cryogels and aerogels has recently been studied **[30-33]**. For most of the conducting polymer composites, the adsorption process is classified as physical sorption, hydrogen bonding, electrostatic or n-n interactions, etc. **[34]**.

In the present work, we report the simple, one-step procedure for the preparation of polyaniline/poly(vinyl alcohol) composite aerogels containing hexaferrite particles. Such conducting and magnetic composites are macroporous and have good mechanical properties, they can be easily handled and prepared in desired shape. The ability of this new composite aerogel to remove organic dye from wastewater was also illustrated on example of anionic Reactive Black 5 dye. Moreover, we demonstrate the possibility to manipulate aerogel using static magnetic field as a proof-of-concept for effective removal of adsorbent from fluidic system **(Fig. 1)**.

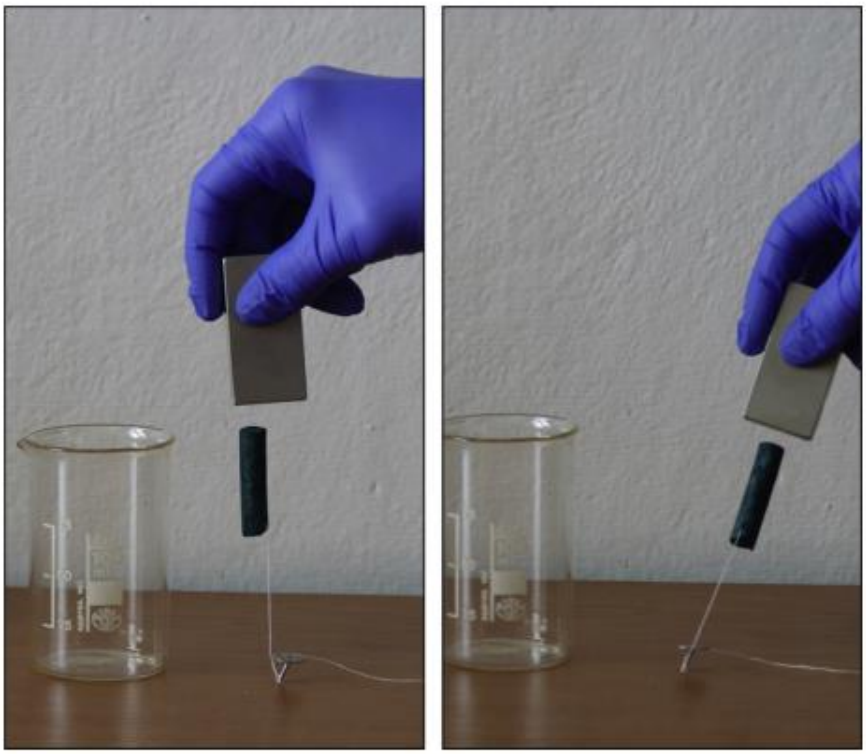

Fig. 1. Attraction of the polyaniline/poly(vinyl alcohol)/hexaferrite aerogel to permanent magnet.

2. Experimental

2.1. Preparation of aerogels

Polyaniline/poly(vinyl alcohol)/hexaferrite (PANI/PVAL/F) cryo-gels were prepared by oxidation of aniline hydrochloride (0.2 M; Penta, Czech Republic) with ammonium peroxydisulfate (0.25 M; Lachner, Czech Republic) in the presence of 5 wt.% of poly(vinyl alcohol) (Mowiol 10-98, Sigma-Aldrich; molecular weight 61,000) in aqueous suspension of hexaferrite particles (Ni_2SrCr_xW hexaferrite, Ferrite Domen Co., St. Petersburg, Russian Federation, 1 or 2wt.%), at 25 °C. The mixture was sucked into a plastic syringe, quickly frozen in solid carbon dioxide/ethanol suspension, and then left in a freezer at -24 °C for 5 days to polymerize [30]. After thawing at room temperature, cryogels were removed from the syringe and immersed in excess of water to extract any residual reactants and by-products. Then PANI/ PVAL/F aerogel was obtained by freeze-drying of corresponding cryo-gels.

2.2. Removal of organic dye

Dye adsorption capability of PANI/PVAL/F was examined by using Reactive Black 5 (Sigma-Aldrich) as a model anionic dye molecule. Reactive Black 5 is a water soluble dye with a characteristic optical absorption maximum at 598 nm. The experiment was carried out using 50 mL of 55 mg L^{-1} Reactive Black 5 solution in which 50 mg of adsorbent was added, without any adjustment of the pH. The mixture was kept under stirring for 4 h at room temperature to attain equilibrium.

2.3 Characterization

Morphology was assessed by JEOL 6400 electron scanning microscope. DC conductivity was obtained by a van der Pauw method on freeze-dried materials compressed to pellets 13 mm in diameter at 70 kN using a hydraulic press Trystom H^{-62}. A Keithley 230 Programmable Voltage Source in serial connection with a Keithley 196 System DMM was used for current measurement and the potential

difference was measured with a Keithley 181 Nanovoltmeter. Measurements were carried out under stable ambient conditions at 23 °C and relative humidity 35 ± 5 %. The conductivity was obtained as an average from the measurements in two perpendicular directions. Static mechanical properties of hydrogels were determined on electromechanical testing machine Instron 6025/5800R equipped with a 10 N load cell at room temperature and with a cross-head speed of 10 mm min^{-1}. Measurement of cylindrical specimens with diameter 4.5 mm and length 60 mm was made on samples immersed in deionized water. Reported values are the averages of at least three measurements. The magnetization curves of neat hexaferrite powder and hexaferrite-filled aerogels were measured on a VSM 7407 Vibrating Sample Magnetometer (Lake Shore, USA) in magnetic fields up to 10kOe. The measurements were carried out at room temperature in air. The amplitude and the frequency of vibration were 1.5 mm and 82 Hz, respectively. The UV-vis spectra were recorded with Lambda 950 spectrometer (Perkin Elmer, UK).

3. Results and discussion

3.1. Morphology

Scanning electron microscopy shows uniform, macroporous structure of neat PANI/PVAL aerogel (Fig. 2a). Hexaferrite particles have a size close to 5 pm (Fig. 2b). They were incorporated inside the aerogel

during the preparation procedure in two fractions, 1 and 2 wt.% relative to swollen hydrogel (PANI/PVAL/1%F and PANI/PVAL/2%F) (Fig. 2c, d). The polyaniline content is ==2wt.%, [30] i.e. comparable with the last hexaferrite fraction, PVAL contribution amounts to 5 wt.%. The remaining part is represented by aqueous phase. Due to large difference in density, however, the volume fraction of hexaferrite is considerably lower than that of polymer part (Fig. 2c, d). To make particles visible, the electron micrographs were taken using back-scattered electrons (Fig. 2c, d). They are present in the PANI/PVAL/1%F and PANI/PVAL/2%F areogels as the white spots (Fig. 2c, d). They are separated from each other and rather randomly distributed inside the composite aerogels. The shape and size of the hexaferrite particles did not change during the preparation of composite aerogels.

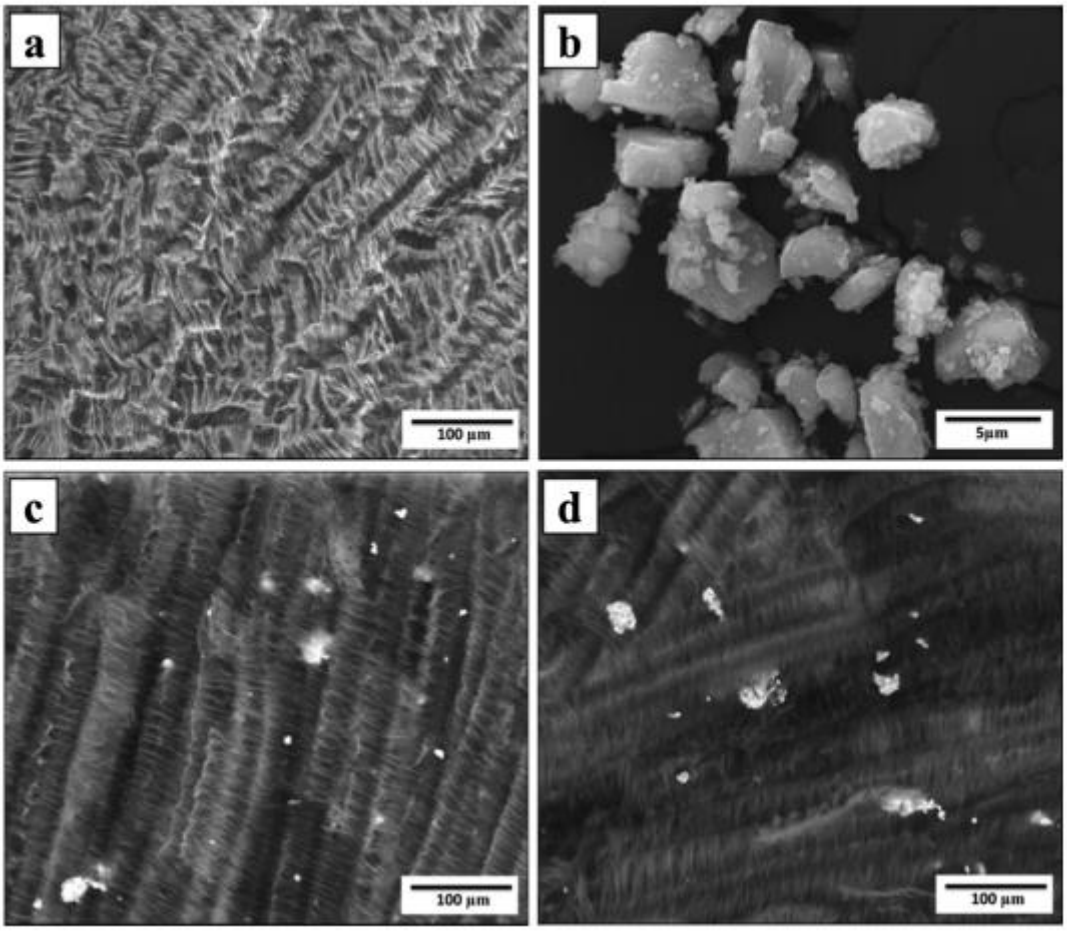

Fig. 2. Scanning electron micrographs of polyaniline/poly(vinyl alcohol) aerogel (a), hexaferrite particles (b), polyaniline/poly(vinyl alcohol) aerogel with 1 wt.% and 2 wt.% of hexaferrite (c) and (d), respectively.

The pore size in aerogels prepared in the presence and in the absence of hexaferrite is substantially different; the pores are smaller in the latter case. The structure of pores is associated with the ice crystals that serve as templates for the polymerization of aniline. We can speculate that the hexaferrite particles act as crystallization nuclei that subsequently affect the structure of ice, and consequently also the microstructure of polymer phase.

3.2. Mechanical properties

The mechanical properties were investigated on gels swollen with water, due to the possible application of such magnetic aerogels in wastewater purification. Neat PANI/PVAL gels possess good mechanical properties **[30]**. The addition of hexaferrite particles to cryogel causes a decrease in strain-at-break and in tensile strength (Table 1). At the same time the Young modulus increased from 47 kPa to =110 kPa. Generally, PANI/PVAL/1%F and PANI/PVAL/2%F composite gels show better resistance to elastic deformation when stress is applied compared to the neat PANI/PVAL gels.

3.3. Conductivity

Conductivity of composites was determined after the compression of aerogels to a pellet. The conductivity of aerogels prepared in the presence of hexaferrite particles is one order of magnitude higher compared with those prepared in their absence (Table 1). The contribution of the hexaferrite to the conductivity of the composite can be neglected, the conducting PANI content is the same in all the composites under study and neither its chemical composition nor the doping level is assumed to be different. The increase in conductivity probably reflects the difference in morphology. As evidenced by Fig. 2 the PANI/PVAL/F composites have more dense s tructure with smaller pores. Such material will assure better connectivity of the conducting PANI phase, which improves the transport of charges in the PANI/PVAL/F composite compared to PANI/PVAL aerogel without hexaferrite.

3.4. Magnetic properties

The room-temperature magnetization curves of neat hexaferrite and PANI/PVAL/F aerogel composites are shown in Fig. 3. The saturation magnetization for aerogel composites is significantly lower, 7.7-12.5 emu g^{-1} compared with hexaferrite particles alone, 40.6 emu g^{-1} that is result of low concentration of magnetic phase in the composite (Fig. 3). The remanent magnetization was similarly reduced, 12.5-15 emu g^{-1}, compared with 35 emu g^{-1} for hexaferrite powder. However, a clearly detectable increase in coercive force from 350 Oe to 415-435 Oe has been observed for aerogels (Fig. 3). High value of coercivity of hexaferrite-contained aerogels guarantees easy removal from wastewater by external magnetic field.

Table 1 Mechanical properties and conductivity of aerogels.

Sample name	Strain-at-break, %	Tensile strength, kPa	Young modulus, kPa	Conductivity, S cm^{-1}
PANI/PVAL	133[a]	12.2[a]	47[a]	0.07
PANI/PVAL/1%F	63	9.2	113	0.22
PANI/PVAL/2%F	59	9	104	0.32

[a]*The data taken from Ref. [30].*

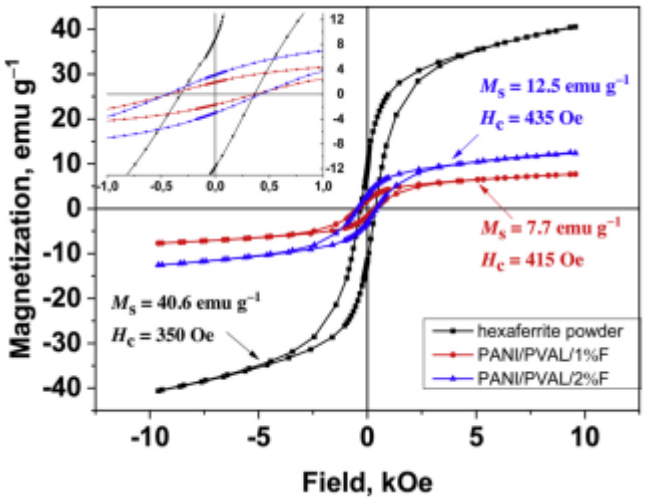

Fig. 3. Magnetization curve of PANI/PVAL aerogel without and with hex-aferrite particles. The inset shows an enlarged view of the magnetization curves showing a coercive force for all three samples.

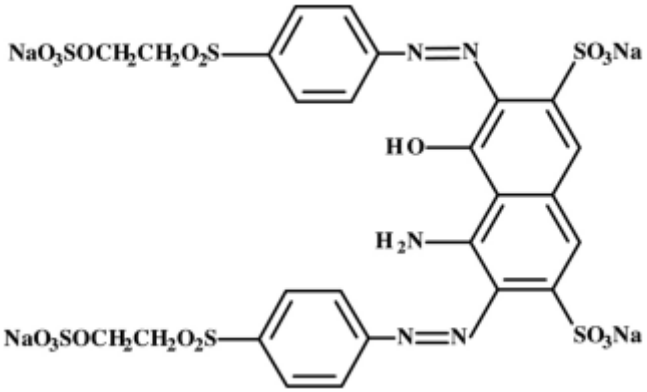

Fig.4. The formula od Reactive Black 5.

The coercive force enhancement can be explained by increase in effective magnetic anisotropy owing to magnetostriction. This assumption has been made on the basis of theoretical and experimental works on the deformation of ferrogels in a uniform magnetic field **[35,36].** To understand the occurrence of magnetostriction in PANI/PVAL/F aerogel composites requires additional investigation, namely polymer-magnetic particles interaction determining the network architecture of aerogels.

Fig. 5. The aqueous solution of Reactive Black 5 becomes colourless after immersion of a magnetic PANI/PVAL/2%F aerogel for 4

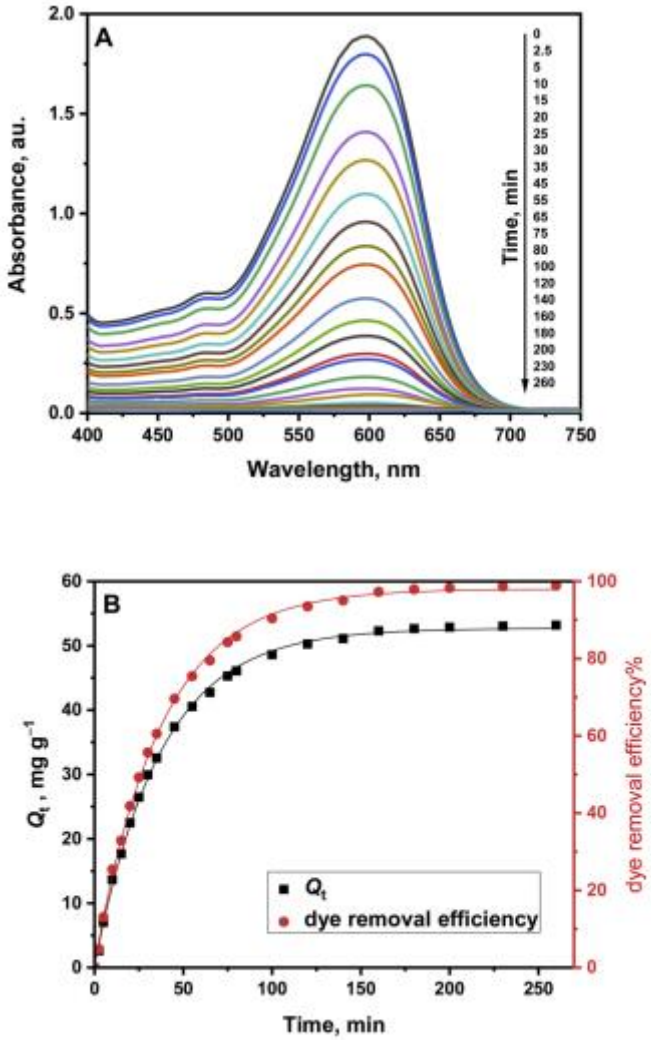

Fig. 6. The change in the optical absorbance of aqueous solution of Reactive Black 5 after introduction of a magnetic PANI/PVAL/2%F aerogel (A), effect of the contact time on the adsorption capacity (Qt) and dye removal efficiency (B). Initial concentration of dye is 55 mgL^{-1}; dosage of PANI/PVAL/2%F aerogel is 50 mg.

3.5. Removal of organic dye by the magnetic aerogel

The materials combining conducting polymers and magnetic component have been used in the design of electromagnetic interference shielding **[10,11]** and in environmental issues, such as water-pollution treatment as dye adsorbents **[37-40]** and as catalysts in photoactalytic degradation of dyes **[41-44].**

It has been established in the literature that conducting polymers adsorb many organic dyes **[28,29]** that are rated as frequent pollutants. The incorporation of a magnetic component allows for an easy separation of adsorbent from the treated medium. Novel materials reported in the present communication, the macroporous aerogels, can well host the hexaferrite particles and, simultaneously, they are efficient dye adsorbers or decomposition photocatalysts. It is not the purpose of this study to provide the detailed study on the extent and mechanism of dye adsorption but rather to illustrate the feasibility of its application in water-pollution treatment on an example of an anionic dye, Reactive Black 5 **(Fig. 4)**.

When the small piece of an aerogel (about = 50 mg) was added to the aqueous solution of a Reactive Black 5 dye (50 mg L^{-1}, 50 mL), the intensive dark blue coloration of the dye solution was substantially reduced after 4 h (Fig. 5). By spectroscopic assay (Fig. 6), the removal of dye was 99 % after 4 h.

4. Conclusions

The conducting poylaniline/poly(vinyl alcohol) cryogels have been prepared by the oxidation of aniline in frozen poly(vinyl alcohol) aqueous solution. The presence of Ni_2SrCr_xW hexaferrite affected the microstructure of hydrogels when the pore size became smaller; the presence of a hexaferrite obviously affected the formation of ice crystals that serve as a template for polyaniline deposition. The macroporous aerogels have been obtained after freeze-drying. After the compression to pellets, they display the conductivity higher by one orders of magnitude compared with a material prepared in the absence of hexaferrite. This is also the consequence of the smaller pore size and resulting better connectivity of the conducting phase. The aerogel has been illustrated to adsorb the organic dye, Reactive Black 5, 99 % after 4 h, and thus be useful in water-pollution treatment. The hexaferrite particles with high value of coercive force allow for the easy separation of adsorbent from aqueous medium. The conductivity and redox properties of polyaniline have not been directly exploited but could be used for the controlled adsorption/desorption by electrochemical switching between the leu-coemeraldine, emeraldine, and pernigraniline oxidation states.

References

[1] H. Ben Fredj, S. Helali, C. Esseghaier, L. Vonna, L. Vidal, A. Abdelghani, Labeled magnetic nanoparticles assembly on polypyrrole film for biosensor applications, Talanta 75 (2008) 740-747.

[2] Z. Shahnavaz, F. Lorestani, Y. Alias, P.M. Woi, Polypyrrole-ZnFe2O4 magnetic nanocomposite with core-shell structure for glucose sensing, Appl. Surf. Sci. 317 (2014) 622-629.

[3] K.G.B. Alves, C.A.S. Andrade, S.L. Campello, R.E. de Souza, C.P. de Melo, Magnetite/polypyrrole hybrid nanocomposites as a promising magnetic resonance imaging contrast material, J. Appl. Polym. Sci. 128 (2013) 3170-3176.

[4] M. Mallouki, F. Tran-Van, C. Sarrazin, P. Simon, B. Daffos, A. De, C. Chevrot, J. Fauvarque, Polypyrrole-Fe2O3 nanohybrid materials for electrochemical storage, J. Solid State Electrochem. 11 (2007) 398-406.

[5] M. Mallouki, F. Tran-Van, C. Sarrazin, C. Chevrot, J.F. Fauvarque, Electrochemical storage of polypyrrole-Fe2O3 nanocomposites in ionic liquids, Electrochim. Acta 54 (2009) 2992-2997.

[6 K. Mohanraju, V. Sreejith, R. Ananth, L. Cindrella, Enhanced electrocatalytic activity of PANI and CoFe2O4/PANI composite supported on graphene for fuel cell applications, J. Power Sources 284 (2015) 383-391.

[7] S. Khilari, S. Pandit, J.L. Varanasi, D. Das, D. Pradhan, Bifunctional manganese ferrite/polyaniline hybrid as electrode material for enhanced energy recovery in microbial fuel cell, ACS Appl. Mater. Interfaces 7 (2015) 20657-20666.

[8] R. Peymanfar, A. Javidan, S. Javanshir, Preparation and investigation of structural, magnetic, and microwave absorption properties of aluminum-doped strontium ferrite/MWCNT/polyaniline nanocomposite at KU-band frequency, J. Appl. Polym. Sci. 134 (2017) 45135.

[9] W. Wang, S.P. Gumfekar, Q. Jiao, B. Zhao, Ferrite-grafted polyaniline nanofibers as electromagnetic shielding materials, J. Mater. Chem. C 1 (2013) 2851-2859.

[10] B.J. Madhu, M. Gurusiddesh, T. Kiran, B. Shruthi, H.S. Jayanna, Structural, dielectric, ac conductivity and electromagnetic shielding properties of polyaniline/ Ni0.5Zn0.5Fe2O4 composites, J. Mater. Sci.-Mater. Electron. 27 (2016) 7760-7766.

[11] M. Abdullah Dar, K. Majid, M. Hanief Najar, R.K. Kotnala, J. Shah, S.K. Dhawan, M. Farukh, Surfactant-assisted synthesis of polythiophene/Ni0.sZn0.5Fe2-xCexO4 ferrite composites: study of structural, dielectric and magnetic properties for EMI-shielding applications, Phys. Chem. Chem. Phys. 19 (2017) 10629-10643.

[12] K. Singh, A. Ohlan, V.H. Pham, R. Balasubramaniyan, S. Varshney, J. Jang, S.H. Hur, W.M. Choi, M. Kumar, S.K. Dhawan, B.-S. Kong, J.S. Chung, Nanostructured graphene/Fe3O4 incorporated polyaniline as a high performance shield against electromagnetic pollution, Nanoscale 5 (2013) 2411-2420.

[13] V. Babayan, N.E. Kazantseva, I. Sapurina, R. Moučka, J. Stejskal, P. Sáha, Increasing the high-frequency magnetic permeability of MnZn ferrite in polyaniline composites by incorporating silver, J. Magn. Magn. Mater. 333 (2013) 30-38.

[14] N.E. Kazantseva, et al., Magnetic particle-filled polymer microcomposites, in: S. Thomas (Ed.), Polymer Composites, vol. 1, Willey-VCH, Weinheim, 2012, pp. 613-669.

[15] R. Suresh, K. Giribabu, R. Manigandan, A. Stephen, V. Narayanan, Fe2O3@poly-aniline nanocomposite: characterization and unusual sensing property, Mater. Lett. 12 (2014) 8369-8372.

[16] D.E. Park, H.S. Chae, H.J. Choi, A. Maity, Magnetite-polypyrrole core-shell structured microspheres and their dual stimuli-response under electric and magnetic fields, J. Mater. Chem. C 3 (2015) 3150-3158.

[17] P. Bober, B.A. Zasoňska, P. Humpolíček, Z. Kuceková, M. Varga, D. Horák, V. Babayan, N. Kazantseva, J. Prokeš, J. Stejskal, Polyaniline-maghemite based dispersion: electrical, magnetic properties and their cytotoxicity, Synth. Met. 214 (2016) 23-29.

[18] B.A. Zasoňska, P. Bober, P. Jošt, E. Petrovský, P. Boštík, D. Horák, Magnetoconductive maghemite core/polyaniline shell nanoparticles: physico-chemical and biological assessment, Colloid Surf. B-Biointerfaces 141 (2016) 382-389.

[19] H. Gu, H. Zhang, C. Ma, S. Lyu, F. Yao, C. Liang, X. Yang, J. Guo, Z. Guo, J. Gu, Polyaniline assisted uniform dispersion for magnetic ultrafine barium ferrite nanorods reinforced epoxy metacomposites with tailorable negative permittivity, J. Phys. Chem. C 121 (2017) 13265-13273.

[20] B.A. Zasoňska, U. Acharya, J. Pfleger, P. Humpolíček, J. Vajďák, J. Svoboda, E. Petrovsky, J. Hromádková, Z. Walterová, P. Bober, Multifunctional polypyrrole@ maghemite@silver composites: synthesis, physico-chemical characterization and antibacterial properties, Chem. Pap. 72 (2018) 1789-1797.

[21] A.A. Farghali, M. Moussa, M.H. Khedr, Synthesis and characterization of novel conductive and magnetic nano-composites, J. Alloys Compd. 499 (2010) 98-103.

[22] D. Mehta, S. Mazumdar, S.K. Singh, Magnetic adsorbents for the treatment of water/wastewater-a review, J. Water Process Eng. 7 (2015) 244-265.

[23] B. Mu, A. Wang, One-pot fabrication of multifunctional superparamagnetic atta-pulgite/Fe3O4/polyaniline nanocomposites served as an adsorbent and catalyst support, J. Mater. Chem. A 2 (2015) 281-289.

[24] A.R. Sadrolhosseini, M. Naseri, S.A. Rashid, Polypyrrole-chitosan/nickel-ferrite nanoparticle composite layer for detecting heavy metal ions using surface plasmon resonance technique, Opt. Laser Technol. 93 (2017) 216-223.

[25] M.S. Zoromba, M.I.M. Ismail, M. Bassyouni, M.H. Abdel-Aziz, N. Salah, A. Alshahrie, A. Memic, Fabrication and characterization of poly (aniline-co-o-anthranilic acid)/magnetite nanocomposites and their application in wastewater treatment, Colloid Surf. A: Physicochem. Eng. Aspects 520 (2017) 121-130.

[26] U.O. Aigbe, R. Das, W.H. Ho, V. Srinivasu, A. Maity, A novel method for removal of Cr(VI) using polypyrrole magnetic nanocomposite in the presence of unsteady magnetic fields, Sep. Purif. Technol. 194 (2018) 377-387.

[27] E.N. Zare, A. Motahari, M. Sillanpaa, Nanoadsorbents based on conducting polymer nanocomposites with main focus on polyaniline and its derivatives for removal of heavy metal ions/dyes: a review, Environ. Res. 162 (2018) 173-195.

[28] B. Yan, Z.H. Chen, L. Cai, Z.M. Chen, J.W. Fu, Q. Xu, Fabrication of polyaniline hydrogel: synthesis, characterization and adsorption of methylene blue, Appl. Surf. Sci. 356 (2015) 39-47.

[29] M.M. Ayad, W.A. Amer, S. Zaghlol, I.M. Minisy, P. Bober, J. Stejskal, Polypyrrole-coated cotton textile as adsorbent of methylene blue dye, Chem. Pap. 72 (2018) 1605-1618.

[30] J. Stejskal, P. Bober, M. Trchová, A. Kovalcik, J. Hodan, J. Hromádková, J. Prokeš, Polyaniline cryogels supported with poly(vinyl alcohol): soft and conducting, Macromolecules 50 (2017) 972-978.

[31] P. Bober, M. Trchová, J. Kovářová, U. Acharya, J. Hromádková, J. Stejskal, Reduction of silver ions to silver with polyaniline/poly(vinyl alcohol) cryogels and aerogels, Chem. Pap. 72 (2018) 1619-1628.

[32] J. Stejskal, P. Bober, Conducting polymer colloids, hydrogels, and cryogels: common start to various destinations, Colloid Polym. Sci. 296 (2018) 989-994.

[33] P. Bober, J. Pfleger, I.A. Pašti, N.M. Gavrilov, S.K. Filippov, D. Klepac, M. Trchová, H. Hlídková, J. Stejskal, Carbogels: carbonized conducting polyaniline/poly(vinyl alcohol) aerogels derived from cryogels for electrochemical capacitors, J. Mater. Chem. A 7 (2019) 1785-1796.

[34] Y. Huang, J. Li, X. Chen, X. Wang, Applications of conjugated polymer based composites in wastewater purification, RSC Adv. 4 (2014) 62160-62178.

[35] P.A. Sanchez, O.V. Stolbov, S.S. Kantorovich, Y.L. Raikher, Modeling the magnetostriction effect in elastomers with magnetically soft and hard particles, Soft Matter 15 (2019) 7145-7158.

[36] P. Ilg, Stimuli-responsive hydrogels by magnetic nanoparticles, Soft Matter 9 (2013) 3465-3468.

[37] M. Bhaumik, H.J. Choi, R.I. McCrindle, A. Maity, Composite nanofibers prepared from metallic iron nanoparticles and polyaniline: high performance for water treatment applications, J. Colloid Interface Sci. 425 (2014) 75-82.

[38] W.L. Guo, F.F. Hao, X.X. Yue, Z.H. Liu, Q.Y. Zhang, X.H. Li, J. Wei, Rhodamine B removal using polyaniline-supported zero-valent iron powder in the presence of dissolved oxygen, Environ. Prog. Suistain. Energy 35 (2016) 48-55.

[39] H.F. Xie, M. Yan, Q. Zhang, H.X. Qu, J.M. Kong, Hemin-based biomimetic synthesis of PANI@iron oxide and its adsorption of dyes, Desalin. Water Treat. 67 (2017) 346-356.

[40] B. Mu, J. Tang, L. Zhang, A.Q. Wang, Facile fabrication of superparamagnetic graphene/polyaniline/Fe3O4 nanocomposites for fast magnetic separation and efficient removal of dye, Sci. Rep. 7 (2017) 5347.

[41] A. Pant, R. Tanwar, B. Kaur, U.K. Mandal, A magnetically recyclable photocatalyst with commendable dye degradation activity at ambient conditions, Sci. Rep. 8 (2018) 14700.

[42] S. Zeng, J. Yang, X.Y. Qiu, Z.Y. Liang, Y.M. Zhang, Magnetically recyclable MnFe2O4/polyaniline compositewith enhanced visible light photocatalytic activity for rhodamine B degradation, J. Ceram. Soc. Japan 124 (2016) 1152-1156.

[43] M.R. Abukhadra, M. Shaban, M.A. Abd El Samad, Enhanced photocatalytic removal of Safranin-T dye under sunlight within minute time intervals using heulandite/ polyaniline@ nickel oxide composite as a novel photocatalyst, Ecotoxicol. Environ. Saf. 162 (2018) 261-271.

[44] R. Tanwar, U.K. Mandal, Photocatalytic activity of Ni0.5Zn0.sFe2O4@ polyaniline decorated BiOCl for azo dye degradation under visible light - integrated role and degradation kinetics interpretation, RSC Adv. 9 (2019) 8977-8993.