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Studies on adsorption capacity of cationic dyes on several magnetic nanoparticles

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Abstract: In this study the dyes used are Basic fuchsin and Methylene blue. The adsorption was studied in relation to the metal in the ferrite, time of exposure and dye concentration. The highest adsorbtion capacity was observed for $MgFe_2O_4$ at a dye concentration of 0.06 mM, adsorption percent of 88% in 3 hours. Desorption was also studied by redispersion in ethanol. The main adsorption mechanism is thought to be through electrostatic interaction, mainly due to surfactant groups present on the nanoparticles. The nanoparticles have ferromagnetic behavior under magnetic field which allows for effective separation.

Keywords: Nanoparticles; Dyes; Adsorption.

Introduction

Dyes and pigments are widely used in the industry, especially in the textile and leather industry as well as plastic, paper or cosmetics

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colorants.[1,2] Basic fuchsin (BF), Methylene blue (MB) and Congo red (CR) are some examples of dyes with cationic structure widely used as coloring agents, also being used in medicine due to their ability to stain certain tissues and bactericidal and their fungicidal properties and can be found as pollutants in wastewater.[3]

Dyes and pigments released into streams present a certain level of toxicity by oxygen adsorption and interfering with light transmission and the photosynthesis process, therefore the necessity of an effective and economically viable wastewater treatment method is an important subject of study.[4] The main methods currently used for dye removal are coagulation,[5] flocculation, and adsorption on active carbon, methods using oxidation and ion exchange, biodegradation, etc. but widespread application of these methods can be restricted due to high cost, difficult disposal and regeneration.[6]

Many absorbents have been studied for the decolorizing of wasterwater.[7] Several studies have reported the use of magnetic ferrite nanoparticles, MFe_2O_4 (M = Mg, Mn, Co, Ni) synthesized by various methods, due to the reduced obtaining cost, high surface area and recovery using their magnetic properties and reutilization of these materials.[3,8]

Moreover nanoparticles synthesized in the presence of a surfactant have additional properties due to the presence of organic groups on the nanoparticles surface.[9] So, the mesoporous ferrites nanocomposites present effective absorption of dyes inside of the porous network.[10] Then, the magnetic nanoparticles and dyes are magnetically separated. The dyes can be released in different solvents such as ethanol, water, and the nanoparticles can be easy separated by using a simple magnet and the catalyst is regenerated.

The aim of this work was to study the adsorption of several cationic dyes on magnetic ferrite nanoparticles MFe_2O_4 (M= Mg, Mn, Co, Ni) synthesized by coprecipitation method.

Results and discussions

The studies on adsorption of cationic dyes on the magnetic nanoparticles have focused on determining the adsorption degree (amount of dye adsorbed on a specific amount of NPs), adsorption speed and determining the degree of desorption. The cationic dyes used are BF and MB. BF is an amine salt with three amine groups, two primary amines and a secondary amine and have a maximum absorption at $\lambda = 543$ nm. The molecular structure is illustrated in Figure 1. MB is a heterocyclic chemical compound used also as a cationic dye with maximum absorption at 670 nm. The molecular structure is illustrated in Figure 2.

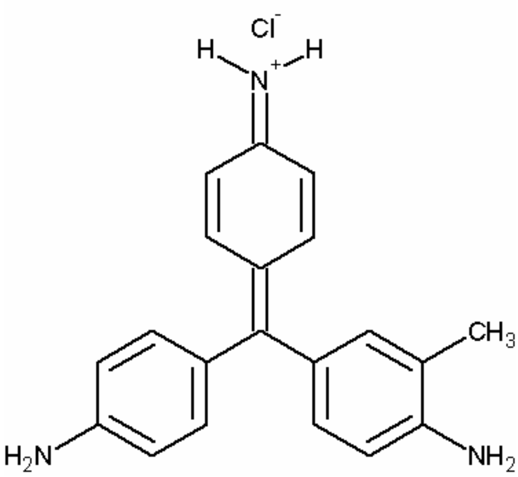

Figure 1. Basic fuchsin structure.

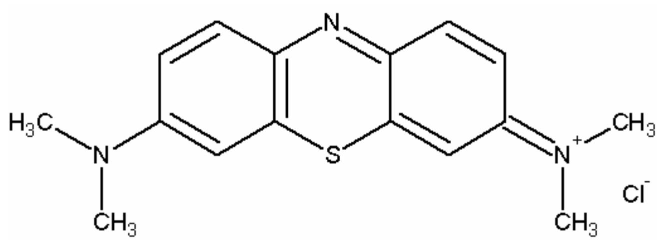

Figure 2. Methylene blue structure.

The UV-Vis spectra of a series of dilutions from the solution of BF and MB were recorded at 543 nm and 670 nm respectively. Good linear fits between *A* and *c* according to Lambert-Beer law have been observed for BF and MB concentrations between 0.01 and 0.06 mM. The UV spectra and fitting linear points is presented in Figure 3.

The linear equations for BF (eq. 1) and MB (eq. 2) are as follows:

$$A= -0.03178+49.8930\cdot c \qquad (1)$$

$$A= 0.21224+46.0542\cdot c \qquad (2)$$

and the linear correlations coefficients are R^2=0.99902 and 0.96812 respectively.

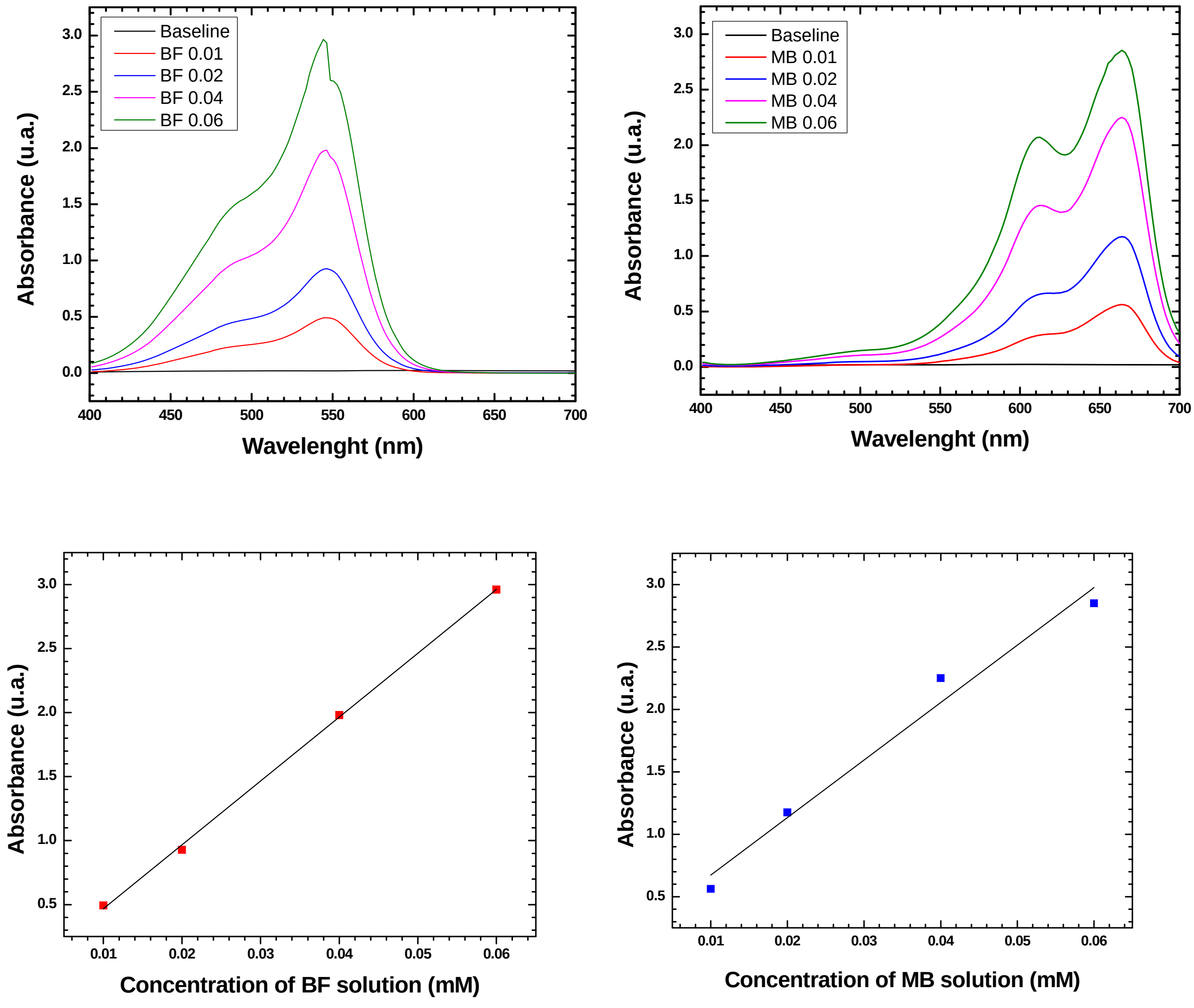

Figure 3. UV spectra and fitting linears of standard BF and MB solution.

Adsorption studies

The degree of adsorption was determined based on the equation (3) [11]:

$$\%Ads.Dyes = \frac{(C_0 - C)}{C_0} \times 100 \qquad (3)$$

where C_0 is initial concentration of dye and C is the final concentration of dye.

The adsorption of dyes on the ferrites function of time is presented in Figure 4 and Figure 5. The adsorption takes place very fast in the first 10 - 20 minutes and then adsorption is moderate or decreases, in some cases, in the later stages of the adsorption most probably due to the large quantity of dye immobilized on the nanoparticles and the electrostatic interactions.

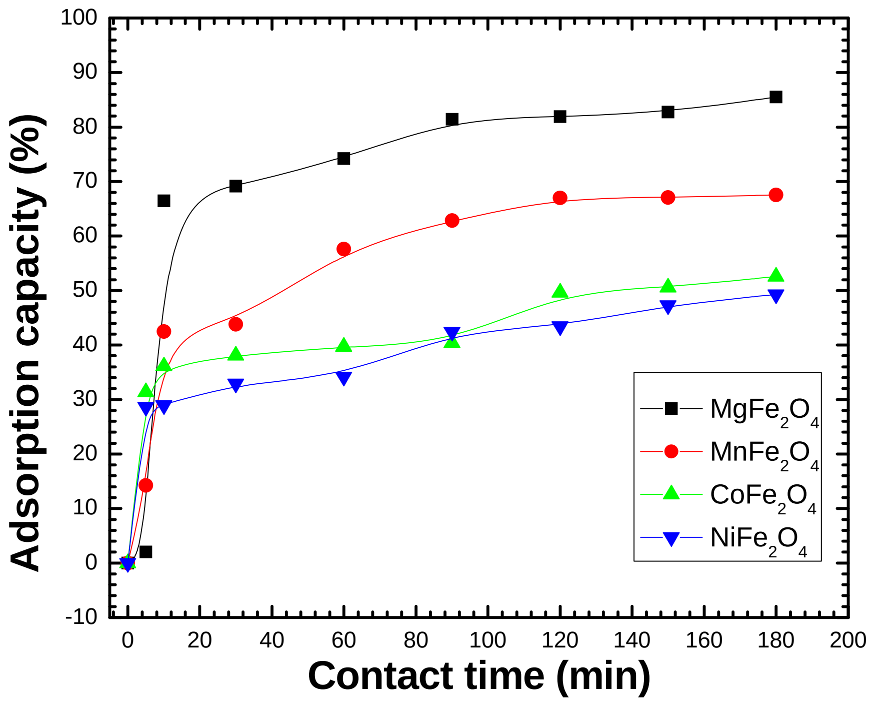

Figure 4. Adsorption of BF on NPs.

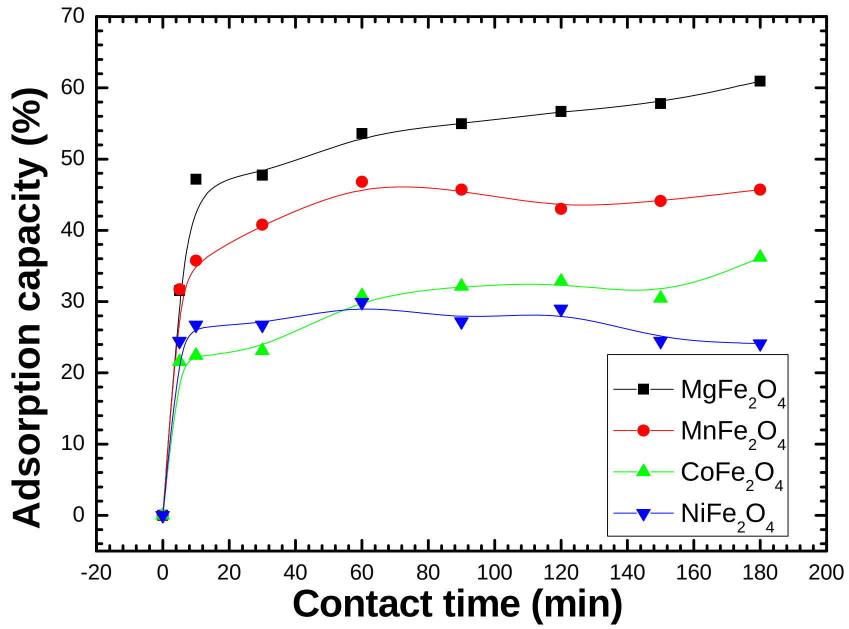

Figure 5. Adsorption of MB on NPs**.**

The results of maximal percent of absorption of dyes on NP`s are presented in Table 1.

Table 1. The maximum level of adsorption of the two dyes on the NP`s.

Dye adsorbed	MFe_2O_4			
	Mg	Mn	Co	Ni
BF (%)	85	66	52	48
MB (%)	57	49	36	29

The nature of divalent metal in the structure of spinel ferrite influences the adsorption capacity. Therefore, the $MgFe_2O_4$ being the most effective with an adsorption of 85% for BF and 57% for MB of the total dye amount in the given conditions.

The initial dye concentration has direct effect on the amount of dye adsorbed on the $MgFe_2O_4$ nanoparticles and the removal effectiveness. The quantity of dye removed on the nanoparticles increases with concentration (up to 50 mg MB /g NP and more than 250 mg BF /g NP) (Figure 6).

The effectiveness (percentage of dye removed) decreases (Figure 7) at concentrations above 0.06 mM for BF and 0.04 mM for MB. The pH of all solutions was that of stock dye solutions and all experiments were performed at room temperature without stirring.

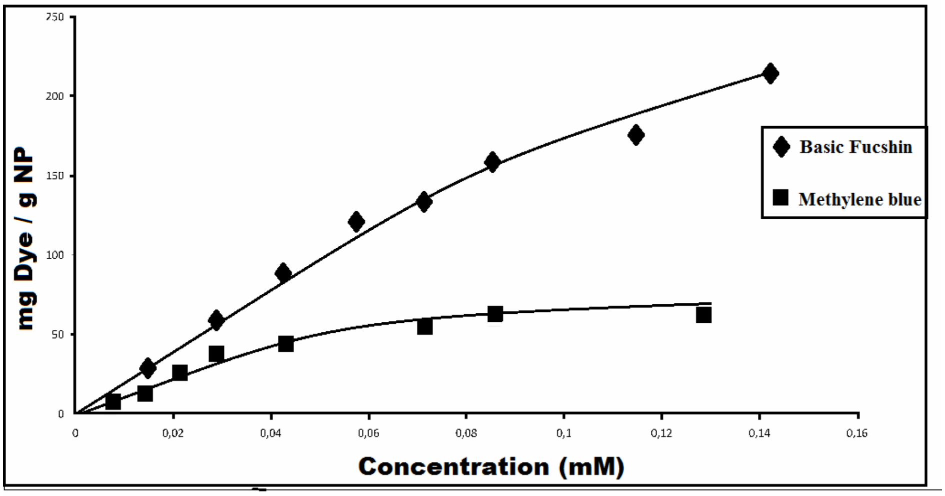

Figure 6. Adsorption capacity.

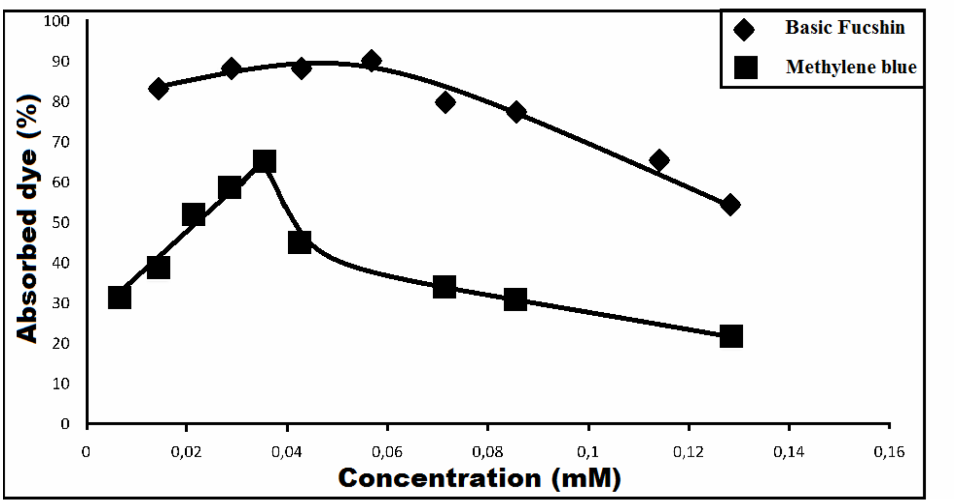

Figure 7. Adsorption effectiveness.

Desorption experiments

The desorption was studied using the previously loaded nanoparticles. The amount of dye on the nanoparticles has been calculated as the difference of the dye concentration in the standard solutions and the concentration after adsorption. The correlation between the amount of dye adsorbed on the nanoparticles and release effectiveness has been studied using nanoparticles loaded with increasing amount of dye. The release of the dye is efficient for methylene blue when the nanoparticles have a small amount of adsorbed dye (87% release for 0.17 mmol/g NP) and less efficient at high amounts of dye loaded on the nanoparticles (21% release for 0.51 mmol/g NP) (Figure 8). BF, which is adsorbed more efficiently by the nanoparticles, tends to remain bonded to the nanoparticles, as suggested from the amount of dye desorbed (less than 20%) even when the loaded amount of dye is small (0.02 mmol/g NP). This difference in adsorption and desorption efficiency indicates than the bond between the nanoparticles and BF is stronger than that with MB.

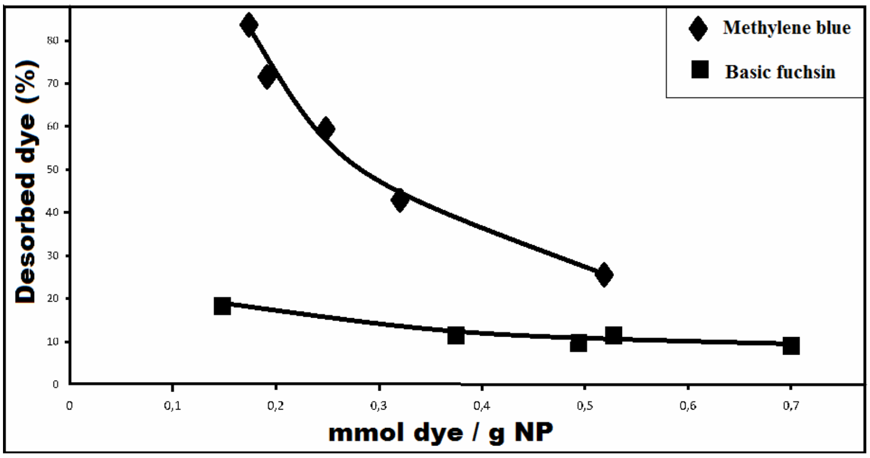

Figure 8. Desorption efficiency.

The mechanism suggested for wastewater treatment is that of fixation of dye through electrostatic interactions and not catalyzed degradation as encountered for numerous dyes. This mechanism is confirmed through FT-IR spectroscopy. The nanoparticles used in the adsorption and desorption studies were magnetically separated, washed with distilled water and ethanol (for those used in the desorption study), slowly dried and analyzed through FT-IR spectroscopy. All the dye's characteristic bands can be clearly observed in the loaded nanoparticles spectrum and that of those used in the desorption study suggesting the presence of the nondesorbed dye (Figure 9). The specific bands for the Mg-O and Fe-O are visible in the lower range wavenumbers (600-400 cm^{-1}). The incomplete desorption is confirmed by FT-IR spectroscopy.

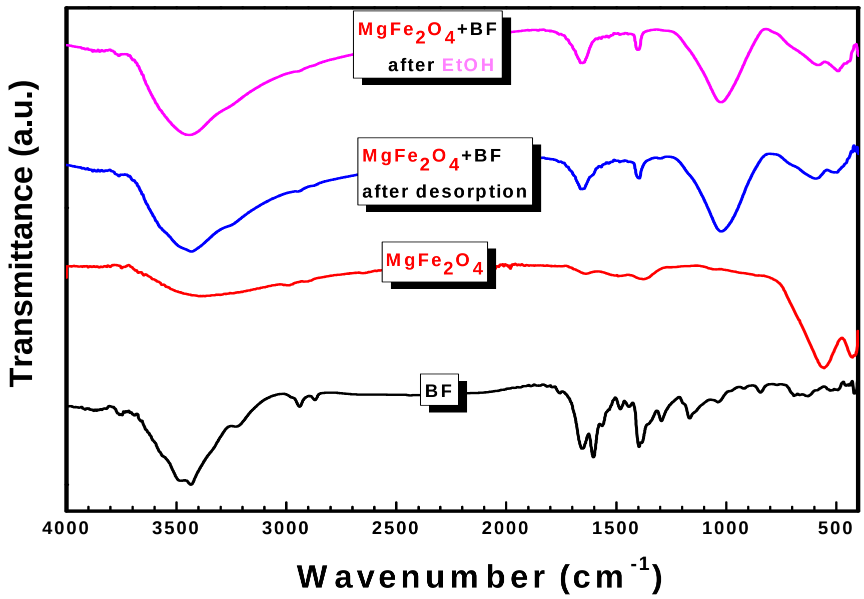

Figure 9. FT-IR spectra of BF, $MgFe_2O_4$, BF loaded on $MgFe_2O_4$ and NPs after adsorption and desorption.

Experimental

Materials and methods

Basic fuchsin, Methylene blue and solvents used were commercially available reagents and used without any purification.

Nanoparticles of MFe_2O_4 (M=Co, Mg, Mn, Ni), MNPs were prepared by coprecipitation method in presence of Linseed Oil such as surfactant.[12,13]

Spectrophotometric measurements were taken on GBC Cintra 101 UV-VIS spectrometer. FT-IR spectra were recorded with Jasco 660 plus FT-IR spectrometer in high purity KBr pellets.

Adsorption experiments

Stock solutions of MB and BF 10^{-3} M were prepared with distilled water and needed concentrations were obtained by diluting the previously prepared solutions with distilled water.

Adsorption capacity, kinetics, influence of metal adsorption capacity and desorption were studied by UV-VIS measurements. Concentrations were determined using a calibration curve obtained by measuring the UV-Vis spectra of predetermined concentrations.

The adsorption capacity was determined for MFe_2O_4 using solutions of increasing concentration and constant nanoparticles concentration solution (1mg/mL) for a contact time of 180 minutes.

The kinetics and the influence of the metal in the ferrite were determined by preparing identical solutions of dye, adding 1mL solution of nanoparticles (1mg/mL) and separating the as prepared samples at specific time intervals of up to 180 minutes for four different MFe_2O_4 (M = Mg, Mn, Co, Ni).

Desorption was studied by redispersing the separated nanoparticles into ethanol, ultrasonification for 1 hour and left under normal conditions for 23 hours followed by spectrometric measurements of the ethanol solution after nanoparticles removal. The magnetic nanoparticles were magnetically separated. The presence of the dye on the nanoparticles after the adsorption and desorption studies was confirmed by FT-IR spectroscopy.

Conclusions

Nanocrystalline MFe_2O_4 (M=Mg, Mn, Co, Ni) synthesized through the coprecipitation method are excellent candidate for treatment of wastewater containing cationic dyes treatment due to the ease of synthesis, low cost, high efficiency and reusability. The adsorption parameters studied were dye concentration, time of contact and ferrite type. Out of the tested nanoparticles $MgFe_2O_4$ seems to be the best candidate with the highest removal efficiency (85% removal for BF and 57% removal for MB), and the possibility to magnetically separate the loaded nanoparticles for desorption in ethanol and reutilization. The amount of dye that can be adsorbed on the $MgFe_2O_4$ nanoparticles is 50 mg MB/ g NP and more than 250 mg BF/ g NP.

Acknowledgements

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References

1. Wang, L.; Li, J.; Wang, Y.; Zhao, L.; Jiang, Q. Adsorption capability for Congo red on nanocrystalline MFe_2O_4 (M = Mn, Fe, Co, Ni) spinel ferrites. *Chem. Eng. J.* **2012**, *181*, 72-79.
2. Eckenrode, H. M.; Jen, S.-H.; Han, J.; Yeh, A.-G.; Dai, H.-L. Adsorption of a Cationic Dye Molecule on Polystyrene Microspheres in Colloids: effect of

Surface Charge and Composition Probed by Second Harmonic Generation. *J. Phys. Chem. B*. **2005**, *109*, 4646-4653.

3. Liu, Q.; Wang, L.; Xiao, A.; Gao, J.; Ding, W.; Yu, H.; Huo, J.; Ericson, M. Templated preparation of porous magnetic microspheres and their application in removal of cationic dyes from wastewater. *J. Hazard. Mater*. **2010**, *181*, 586-592.
4. Iram, M.; Guo, C.; Guan, Y.; Ishfaq, A.; Liu, H. Adsorption and magnetic removal of neutral red dye from aqueous solution using Fe_3O_4 hollow nanospheres. *J. Hazard. Mater*. **2010**, *181*, 1039-1050.
5. Majcen-Le Marechal, A.; Slokar, Y. M.; Taufer, T. Decoloration of chlorotriazine reactive azo dyes with H_2O_2/UV. *Dyes Pigm.* **1997**, *33*, 281-298.
6. Wu, J. S.; Liu, C. H.; Chu, K. H.; Suen, S. Y. Removal of cationic dye methyl violet 2B from water by cation exchange membranes. *J. Membr. Sci.* **2008**, *309*, 239-245.
7. Mohamed, R. M.; Rashad, M. M.; Haraz, F. A.; Sigmund, W. Structure and magnetic properties of nanocrystalline cobalt ferrite powders synthesized using organic acid precursor method. *J. Magn. Magn. Mater.* **2010**, *322*, 2058-2064.
8. Tai, Y.; Wang, L.; Fan, G.; Gao, J.-M.; Yu, H.; Zhang, L. Recent research progress on the preparation and application of magnetic nanospheres. *Polym. Int.* **2011**, *60*, 976-994.
9. Naseri, M. G.; Saion, E. B.; Ahangar, H. A.; Shaari, A. H. An Overview on Nanocrystalline $ZnFe_2O_4$, $MnFe_2O_4$, and $CoFe_2O_4$ Synthesized by a Thermal Treatment Method. *Mater. Res. Bull.* **2013**, *48*, 1439-1446.
10. Sahoo, B.; Sahu, S. K.; Nayak, S.; Dhara, D.; Pramanik, P. Fabrication of magnetic mesoporous manganese ferrite nanocomposites as efficient catalyst for degradation of dye pollutants. *Catal. Sci. Tech.* **2012**, *2*, 1367-1374.
11. Rahimi, R.; Kerdari, H.; Rabbani, M.; Shafiee, M. Synthesis, characterization and adsorbing properties of hollow Zn-Fe_2O_4 nanospheres on removal of Congo red from aqueous solution. *Desalination.* **2011**, *280*, 412-418.
12. Gherca, D.; Cornei, N.; Mentré, O.; Kabbour, H.; Daviero-Minaud, S.; Pui, A. In situ surface treatment of nanocrystalline MFe_2O_4 (M=Mg, Mn, Co, Ni) spinel ferrites using linseed oil. results to be published (2013).
13. Gherca, D.; Pui, A.; Cornei, N.; Cojocariu, A.; Nica, V.; Caltun, O. Synthesis, characterization and magnetic properties of MFe_2O_4 (M=Co, Mg, Mn, Ni) nanoparticles using ricin oil as capping agent. *J. Magn. Magn. Mater.* **2012**, *324*, 3906-3911.