
Nanosized NiFe₂O₄/ Active Carbon Composite as Adsorbent for Azo Dyes and Colours

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Abstract: Much attention has been paid on nanomaterials in recent years due to their fundamental and technological applications. The physical and chemical properties of nanomaterials have been enhanced because of their surface-to-volume ratio. Spinel ferrite with the general formula of MFe₂O₄ (M is a divalent cation) have attracted much attention because of their interesting properties. Nickel ferrite (NiFe₂O₄) nanocrystalline is one of the most important ferrites among other ferrites because of most promising applications in storage devices, microwave devices, gas sensors, ferrofluids, catalysts and adsorbent. The NiFe₂O₄ nanocrystalline has been synthesized by various methods such as co-precipitation, sonochemical process, polymeric precursor techniques, mechanical alloying, sol-gel, pulsed wire discharge, shock wave, reverse micelles, hydrothermal and ultrasonically assisted hydrothermal processes. In this study NiFe₂O₄ nanoparticels have been prepared by co-precipitation method over active carbon. The composite nanosized NiFe₂O₄/active carbon has been used to remove a number of Azo dyes, such as Alizarine Yellow R and Methyl Orange, from water. The study showed that this composite has a high adsorptive activity for these dyes and its tendency for removal of anionic dye and cationic azo dye was higher than the other. The effect of pH on the rate of the adsorption of the dyes by this ferrite composite was also investigated. The adsorption of these azo dyes on free active carbon and free nanoscaled NiFe₂O₄ was also examined and compared with that of NiFe₂O₄/ active carbon composite. The obtained results revealed that this composite is a superior adsorbent compared with either NiFe₂O₄ or active carbon alone.

Keywords: Nanosized, NiFe₂O₄/Active Carbon, Azo Dyes, Adsorbent

1. Introduction

The study of spinel ferrite is of great importance from both the fundamental and the applied research point of view. High resistivity, low dielectric losses, mechanical toughness and chemical stability make them very promising candidates for high frequency applications [1-4]. And as most of then properties needed for ferrite application are not intrinsic but extrinsic, the preparation of ferrites with optimized properties has always demanded delicate handling and cautious approach. The ferrite is not completely defined by its chemistry and crystal structure. So, in order to reduce the losses many parameters such as density, grain size, porosity and their intra and intergranular distribution must be controlled [5]. Optimum sintering temperature is of great importance assintering influences both densification and grain growth and many magnetic and electrical properties benefit from both a high relative density and a small grain size. This opens the doors for tailoring given properties by careful synthesis of the

building blocks (atoms and molecules) and their assembly to fabricate functional materials with improved properties. This new class of materials is used in important applications such as high frequency transformers Ferro fluids, pigments in paints and ceramics, biomedical applications like drug delivery system hyperthermia, NMR, high density magnetic recording, varistors and dye-sensitized solar cells [6-10]. Ferrites of the type MFe₂O₄ (M is a divalent metal cation) are magnetic materials with cubic spinel structure, which have been extensively used in various technological applications in the past decades [12, 13]. Recently, the exploitation of MnFe₂O₄ and CuFe₂O₄ ferrite in treatment for water has been mostly studied by Qu's group, which exhibited the excellent adsorptive properties with the highly effective recovery of the magnetic separation technique [14-17]. Azo dyes are both the largest and most important group of synthetic dyes. In making the azo linkage, many combinations are possible. These combinations give rise to dyes with a broad range of colors, encompassing yellows, oranges, reds, browns, and blues. NiFe₂O₄ structure is inverse spinel, To the best of our

knowledge, little work has been done on the preparation of activated carbon/NiFe₂O₄ composite and their dye, removal from water. In the present study herein, a simple one-pot refluxing method was employed to develop a new kind of chemical adsorbent, activated Carbon/NiFe₂O₄ composite (AC/NFO).

2. Experimental Details

All the reagents were of analytical grade and used as received without further purification. Nickel nitrate [Ni(NO₃)₂.6H₂O], ferric nitrate [Fe(NO₃)₃.9H₂O], sodium hydroxide (NaOH), activated carbon (AC) and methyl orange (C₁₄H₁₄N₃NaO₃S; MW : 327.33 g mol⁻¹; λ_{max} : 475 nm), Alizarine Yellow R (C₁₃H₉N₃O₅; MW : 287.23 g mol⁻¹).

Activated carbon/NiFe₂O₄ composite was synthesized by a facile refluxing route in alkaline solution. In a typical procedure a certain amount of activated carbon was added into a 150 ml alkaline solution containing 3.4 g NaOH, and stirred at room temperature for 30 min to get the activated carbon suspension. The suspension was then maintained at 100 °C to keep boiling state. 50 ml from metal nitrate aqueous solution was prepared by dissolving Fe(NO₃)₃.9H₂O (5.4944 g) and Ni(NO₃)₂.6H₂O (1.9774 g) in distilled water. The solution was poured as quickly as possible into the above boiling suspension. The mixture solution was then refluxed at 100 °C for 2 h. By a simple magnetic procedure, the resulting product was separated from water and dried at 80 °C for 12 h. The final samples were then confirmed by different techniques as XRD – TEM – etc.

3. Results and Discussion

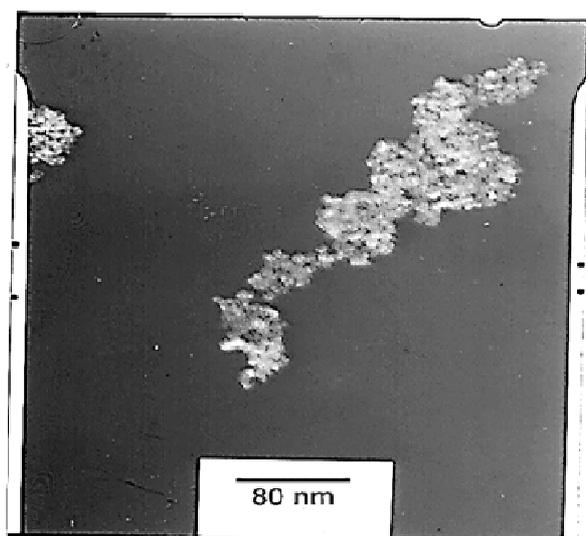


Fig. 1. Image of TEM of AC/NFO in 973 K.

The morphology of the as-prepared AC/NFO was investigated by TEM observations. As shown in Fig.1, it can be seen that NiFe₂O₄ particles deposited on the surface of activated carbon in the composite are uniform with the particle size in the range of 12–14 nm. The average crystallite size of

NiFe₂O₄ particles can be estimated according to the diffraction reflections by using the Debye–Scherrer equation:

$$D = K \lambda / \beta \cos \theta$$

where D is the average crystalline size, K is the so-called shape factor which usually takes a value of about 0.9 and λ is the wavelength of Cu Kα, β is the full width at half maximum (FWHM) of the diffraction peaks, and θ is the Bragg's angle. The average crystallite sizes are estimated to be 21 and 15 nm, respectively, for NiFe₂O₄ particles and NiFe₂O₄ particles in AC/NFO.

The XRD patterns of the calcined NiFe₂O₄ samples are shown in Fig.2. All of the detectable peaks are indexed as NiFe₂O₄ with an inverse spinel structure, as shown in the standard data (JCPDS: 10-0325). No diffraction peaks of other impurities such as α-Fe₂O₃ or NiO were observed. It is clearly seen that the reflection peaks become sharper and narrower with increasing calcination temperature, indicating the enhancement of crystallinity. The average crystallite sizes of NiFe₂O₄ samples were calculated from X-ray line broadening of the reflections of (311), (400), (511) and (440) using Scherrer's equation ($D = 0.89k/(b \cos \theta)$), where k is the wavelength of the X-ray radiation, D is a constant taken as 0.89, θ is the diffraction angle and b is the full width at half maximum (FWHM) [17], and were found to be 54 ± 29 , 68 ± 32 and 107 ± 17 nm for the NiFe₂O₄ samples calcined at 973 K, respectively.

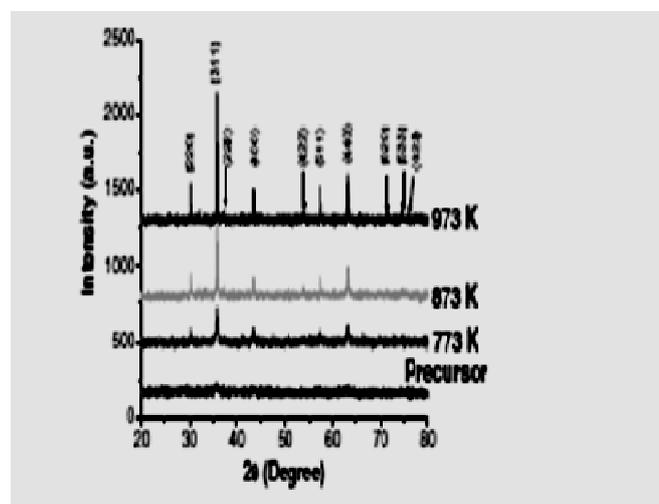
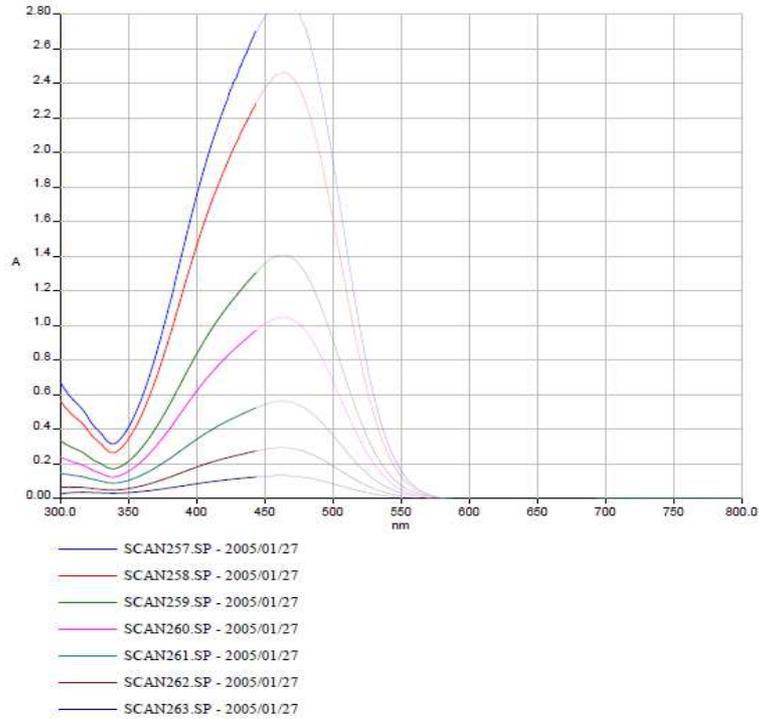


Fig. 2. XRD patterns of the precursor and nanocrystalline NiFe₂O₄ samples calcined in oven at 973K for 3 h.

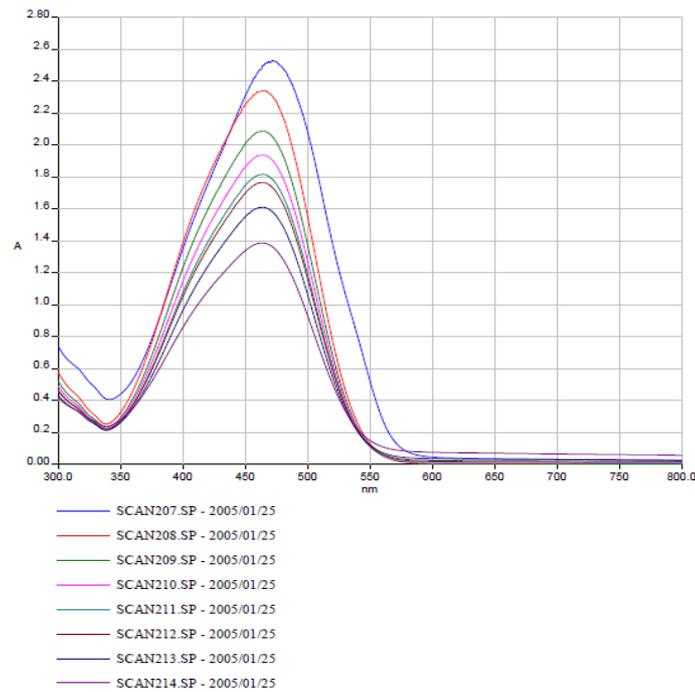
The pH of the dye solutions plays an important role in the whole adsorption process. To determine the optimum pH conditions for adsorption of dyes onto AC/NFO, the effect of solution pH on the adsorption of dyes is investigated in the range of 4-8 with a fixed initial concentration (10⁻⁴ M) and contact time (50 min) and value of AC/NFO was 0.02 g. Graphs of adsorption (UV-VIS) of Methyl orange (for example) by AC/NFO as shown in figures of 3-a, 3-b, 3-c for environments of acidic, base and almost neutral, and as shown in Fig.6. every graph is obtained each 10 min. That remove of

dye by adsorbent in pH of 6.5(almost , neutral) is the most greate , then state of base and at least state of acidic .For example: The adsorption of Methyl orang by AC/NFO present a relatively low at pH of less than 4, and increase up to pH=6. pH of Solution may affect both aqueous chemistry and surface

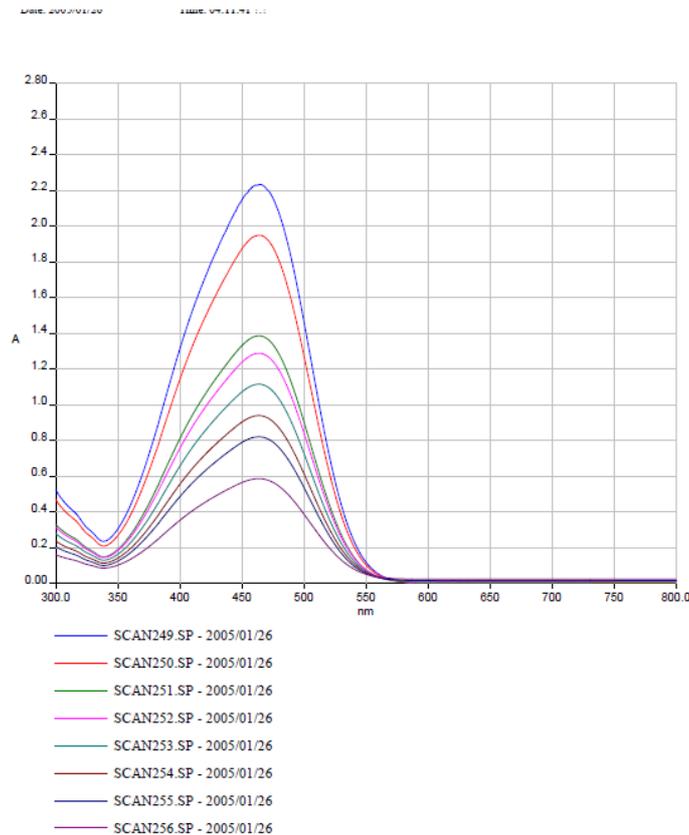
binding-sites of the adsorbent. The decrease of adsorption at pH of less than 4 can be explained that at this acidic pH, ion of H+ may competes with dye ions for the adsorption sites of adsorbent, thereby inhibiting the adsorption of dye , also ferrite was synthesis by NaOH .



a) (fig. 3)



b) (fig. 3)



c) (fig. 3)

Fig. 3. graph of UV-VIS for Methyl orang 10⁻⁴ M by 0.02g of AC/NFO in environments of: a) neutral : pH = 6.5 b) acidic : pH = 4 c) base : pH = 8.

In fig . 4. is shown effect of pH on adsorption of Methyl orang onto AC/NFO to contact time is 50 min and C0 is 100mg L⁻¹ in here .

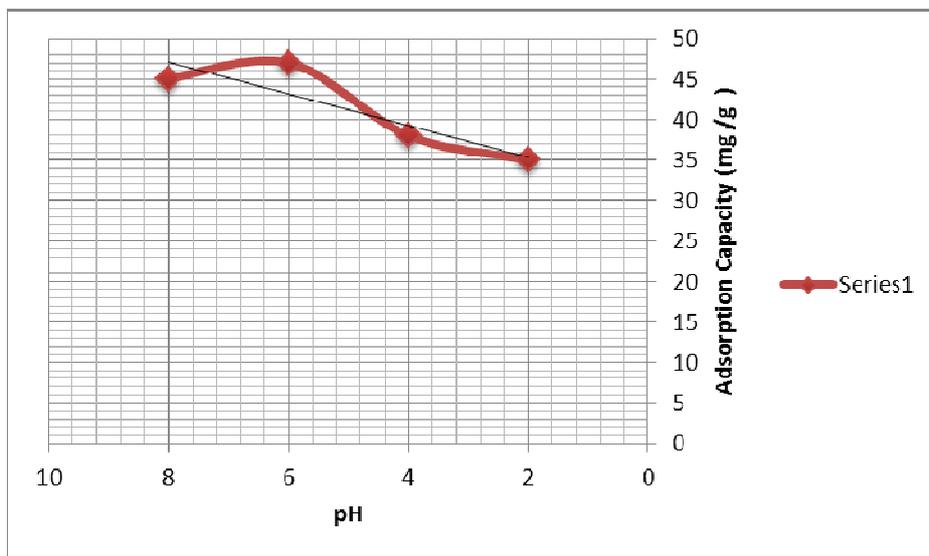


Fig. 4. Effect of pH on adsorption of Methyl orang onto AC/NFO (C0: 100mg L⁻¹; contact time: 50 min).

Azo dyes are widely used in many industrial fields, such as textile, leather, paper, plastics, rubber, etc. They have been considered as an extremely important pollutant in environment due to their complex composition, high toxicity, poor degradability and great solubility in water [18].

Methyl orange is an anionic azo dye (Fig.5.) and Alizarine Yellow R is a cationic azo dye (Fig.6.). in this study; Adsorption of anionic azo dye and cationic azo dye is alike.(Fig.7.).

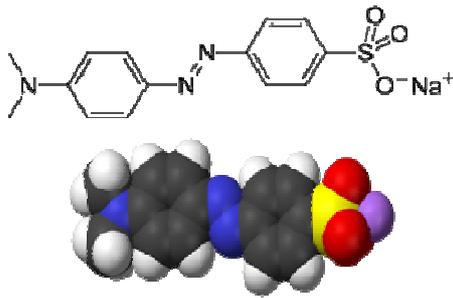


Fig. 5. Methyl orange.

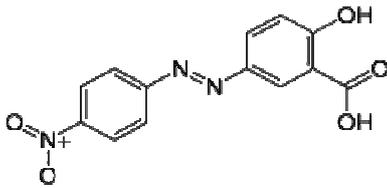


Fig. 6. Alizarine Yellow R.

Adsorption of Methyl orange (anionic azo dye) is all right by AC/NFO because the ion pair formation between anionic azo dye, Methyl orange, and conventional cationic surfactants with different chain lengths, head groups and counter ions.

In the present study, AC/NFO is a good adsorbent because it on its surface has ions of Fe^{3+} (ferrite has spinel structure) that adsorption of anionic azo dye does easily (Fig 7).

On the one hand, Alizarine Yellow R on as a cationic azo dye adsorbate as well as by AC/NFO because ions of OH^- on surface of ferrite have link up with part of cationic from Alizarine Yellow R (Fig.7).

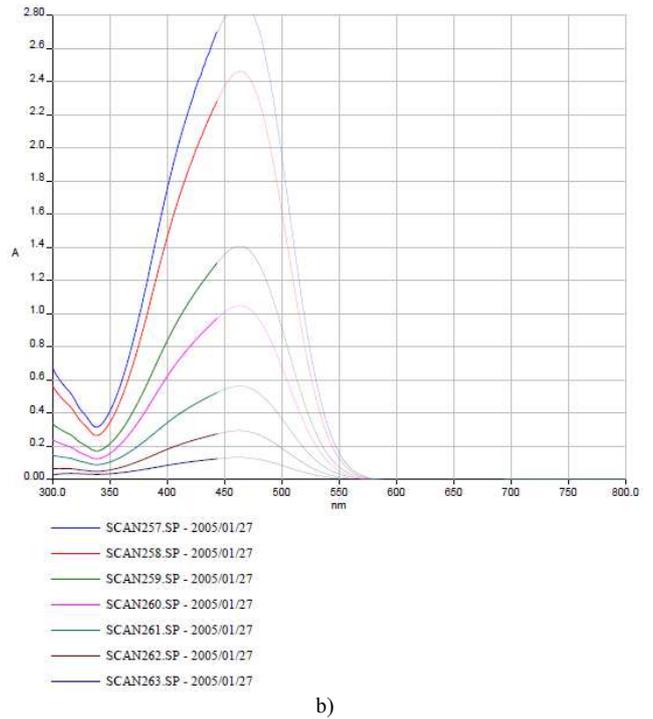
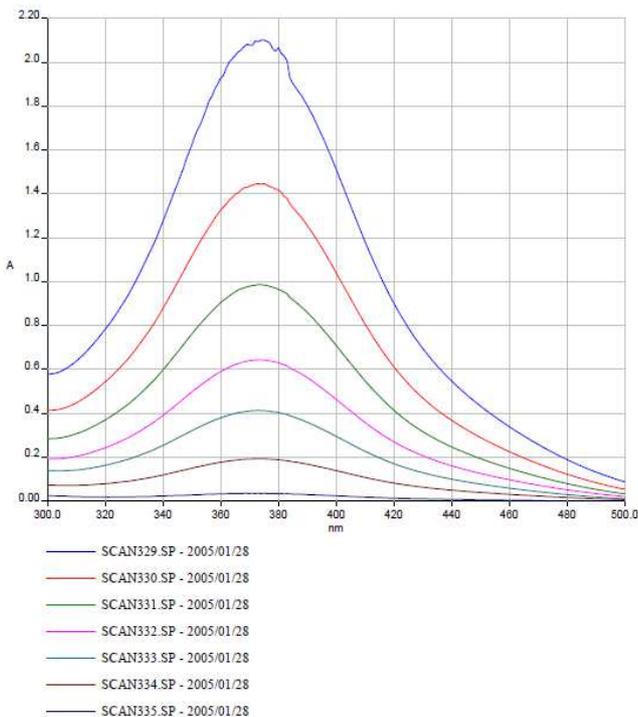
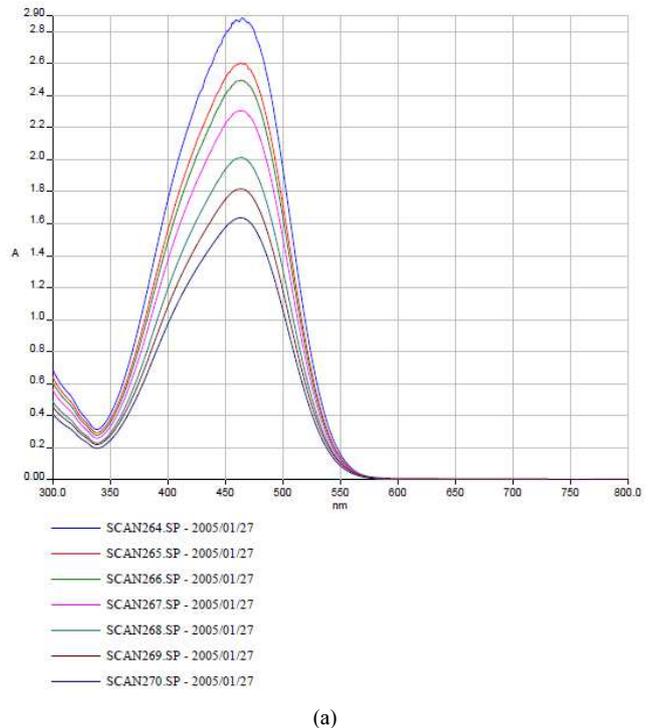


Fig. 7. graph of UV-VIS for Adsorption of dyes (a- Alizarine Yellow R b-Methyl orange) 10^{-4} M by 0.02g of AC/NFO.



a)



(a)

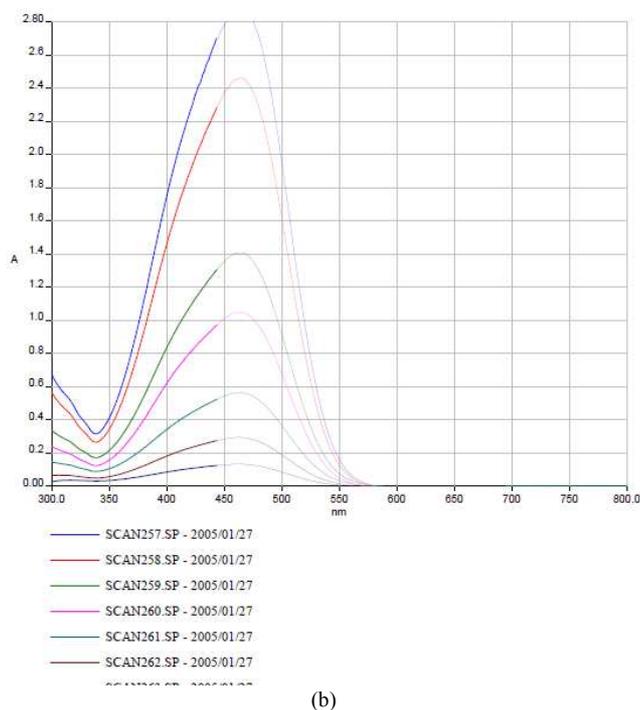
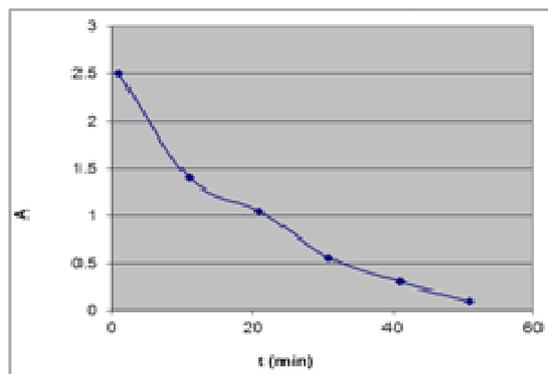
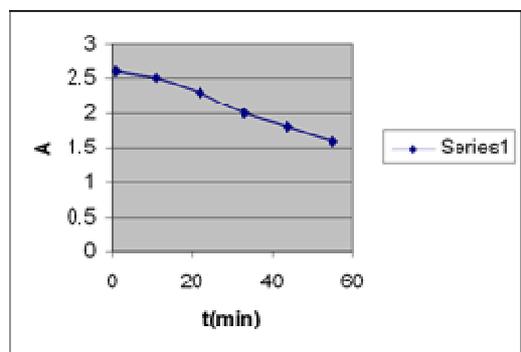


Fig. 8. graph of UV-VIS for Methyl orang 10⁻⁴ M by 0.02g of a) Nickel ferrite b) AC/NFO.



A



B

Fig. 9. graph of adsorption-time for Methyl orang 10⁻⁴ M with A) AC/NFO B) Nickel ferrite.

For example, adsorption of Methyl orang from water is

purpose , that Nickel ferrite adsorption is few but remove Methyl orang from water by AC/NFO is very good also 0.02g AC/NFO was adsorbed dye in 50 min completely , graphs of UV-VIS is existing for Nickel ferrite and AC/NFO , that is showed in figure 8-a and 8-b the effect of contact time on adsorption of Methyl orang onto AC/NFO Nickel ferrite are investigated for initial dye concentration, as shown in Fig.9 for concentrations of 10⁻⁴ M from Methyl orang, value of adsorbent of used was 0.02 g. Adsorption of Methyl orang did by AC/NFO because Methyl orang is a anionic day and surface of AC/NFO is including of Fe³⁺ that has been remained from synthesis of alkalin , therefore adsorption be completed.

4. Conclusion

In this study, Activated carbon/NiFe₂O₄ composite (AC/NFO) was successfully synthesized by a facile one-step refluxing route. The XRD, TEM, surface area were used to characterize the as-prepared composite. The adsorption of dye of azo as Methyl orang onto AC/NFO was investigated and The equilibrium of adsorption of Methyl orang onto AC/NFO was suitably described by the chemical model . The process of adsorption was relatively rapid and was best described by chemical model. AC/NFO adsorbent could be used as a promising and effective adsorbent.

Acknowledgements

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References

- [1] L. J. Berchmans, R.K. Selvan, P.N. Selva Kumar, C.O. Augustin, J. Magn. Mater. 279 (2004) 103 .
- [2] A.M. Shaik, S.S. Bellad, B.K. Chougule, J . Magn. Mater. 195 (1999) 384.
- [3] B. P. Rao, K.H. Rao, K. Trinadha, O.F. Caltunb , J. Optoelectron. Adv. Mater. 6(2004) 951.
- [4] I.Z. Rahman, T.T. Ahmed, The 2nd international conference on structure, processing and properties of materials, Dhaka, Bangladesh 2004.
- [5] K. Ishino Y. Narumiya, Ceram. Bull. 66 (1987) 1469 .
- [6] N. Iftimie, E. Rezlescu, P.D. Popa, N. Rezlescu , J. Optoelectron. Adv. Mater. 7 (2005) 911.
- [7] C. Xu., T. Jun, N. Miura, N. Yamazo, Chem Lett. 3 (1990) 441.
- [8] N. Rezlescu, E. Rezlescu, F. Tudorache, P. D. Popa, J. Optoelectron. Adv. Mater. 6 (2005) 695
- [9] C. Doroftei, N. Rezlescu, E. Rezlescu, P. D Popa, J. Optoelectron. Adv. Mater. 8 (2006) 1012 .
- [10] H. Gleiter, Prog. Mater. Sci. 33 (1989) 223.

- [11] B. Baruwati, M. N. Nadagouda, R. S. Varma, Bulk synthesis of monodisperse ferrite nanoparticles at water–organic interfaces under conventional and microwave hydrothermal treatment and their surface functionalization, *J. Phys. Chem. C* 112 (2008) 18399–18404.
- [12] Q. Song, Z. J. Zhang, Shape control and associated magnetic properties of spinel cobalt ferrite nanocrystals, *J. Am. Chem. Soc.* 126 (2004) 6164–6168.
- [13] G. Zhang, H. Liu, R. Liu, J. Qu, Removal of phosphate from water by a Fe–Mn binary oxide adsorbent, *J. Colloid Interface Sci.* 335 (2009) 168–174.
- [14] G. Zhang, J. Qu, H. Liu, R. Liu, R. Wu, Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal, *Water Res.* 41(2007) 20-27.
- [15] R. Wu, J. Qu, Removal of water-soluble azo dye by the magnetic material MnFe₂O₄, *J. Chem. Technol. Biotechnol.* 80 (2005) 20–27.
- [16] R. Wu, J. Qu, H. He, Y. Yu, Removal of azo-dye Acid Red B (ARB) by adsorption and catalytic combustion using magnetic CuFe₂O₄ powder, *Appl. Catal. B* 48 (2004) 49-5
- [17] B. D. Cullity, S.R. Stock, *Elements of X-ray Diffraction*, third ed., Prentice-Hall, Englewood Cliffs, NJ, 2001
- [18] Ramakrishna et al., 1997; Vandevivere et al., 1998; Robinson et al., 2002