

*Full Length Research Paper*

# MnFe<sub>2</sub>O<sub>4</sub>/bentonite nano composite as a novel magnetic material for adsorption of acid red 138

Saeedeh Hashemian

Islamic Azad University, Yazd branch, Chemistry department, Iran, Yazd. E-mail: Sa\_hashemian@yahoo.com. Tel: 098 351 8211391-9 (572). Fax: 098 3516240020.

Accepted 7 October, 2010

**Magnetic MnFe<sub>2</sub>O<sub>4</sub>/bentonite nanocomposite was synthesized by chemical co-precipitation method. The product was characterized by X-ray diffraction (XRD) and Scanning electron microscope (SEM). XRD results indicated the presence of free quartz in bentonite. The magnetic ferrite MnFe<sub>2</sub>O<sub>4</sub> has spinel structure. It is also found that the presence of bentonite in the magnetic composite has not made any changes in the spinel structure of MnFe<sub>2</sub>O<sub>4</sub>. SEM images of the sorbent shows nanocomposite with a uniform structure and nanochannels from 0.3 to 0.8 μm in diameter having a surface area of 130 m<sup>2</sup> g<sup>-1</sup>. The results also revealed that the composite has much higher catalytic activity than the bentonite. The process confirmed very fast kinetic and pseudo-second-order model for acid red 138 (AR138) from aqueous solutions. The adsorption of AR138 was strongly dependent on the pH of the medium, where the removal efficiency increased as the pH decreased in pH 2.**

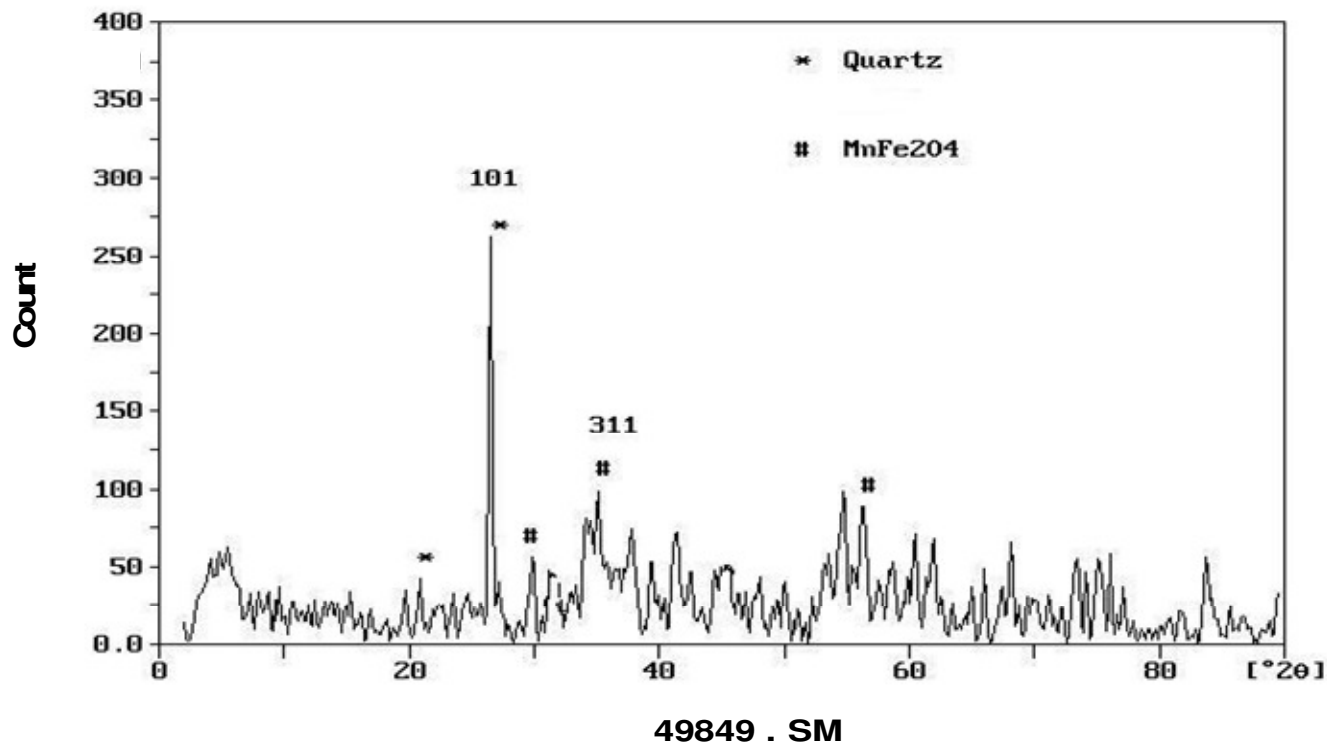
**Key words:** Acid Red 138, adsorption, bentonite, magnetic material, nanocomposite.

## INTRODUCTION

Dyes are aromatic organic colorants having potential applications in paper and in textile industries. One of the major problems concerning textile wastewaters is color effluent. This wastewater contains a variety of organic compound and toxic substances, which are harmful to fish and other aquatic organism. The methods such as coagulation, chemical oxidation, membrane filtration, chemical precipitation and osmosis have not been very successful because dyes are stable to light, oxidizing agents, high capital cost and operational costs.

Adsorption has gained favor in recent years due to proven efficiency in the removal of pollutants from effluents to stable forms for the above conventional methods (Hashemian, 2009). Activated carbon is a widely used adsorbent due to its high adsorption capacity, high surface area, microspores structure and high degree of surface reactivity, but there are some problems with its use. It is expensive and regeneration using solution procedures requires a small additional effluent, while regeneration results in 10 - 15% loss of adsorbent and its uptake capacity and therefore this adds to the operational costs. This leads to a search for cheaper, easily obtainable materials for the adsorption of dye (Garg, 2005, 2008; Kavitha and Namasivayam 2007; Sud, 2008; Hashemian, 2007, 2008; Robinson, 2002; Namasivayam,

2001; Ho, 2004). Natural clays are low-cost and readily available materials functioning as excellent cation exchangers. The adsorption capacity of clays results from a relatively high surface area and a net negative charge on their structure, which attracts and holds cations such as heavy metals (Khenifi, 2007; Oliveira, 2003). The application of magnetic particle technology to solve environmental problem is also considered. Magnetic particles can be used to adsorb contaminants from aqueous or gaseous effluents and after the adsorption is carried out, the adsorbent can be separated from the medium by a simple magnetic process. Therefore, there has been a growing interest in inexpensive high surface area materials, especially metal oxides, due to their unique application, including adsorption and chemical catalysis (Wu and Qu, 2005). Most of these materials have the drawbacks of small adsorption capacity and narrow application range. For example, MnFe<sub>2</sub>O<sub>4</sub> powder and MnO-Fe<sub>2</sub>O<sub>3</sub> composite could only be used to adsorb ionic organic pollutants. In addition, the applicable pH range of these materials was relatively narrow (Wu and Qu, 2005). To overcome the disadvantages of sorbents and magnetic particles, several methods such as impregnation, ball milling and chemical coprecipitation, have been developed to combine them together to produce magnetic



**Figure 1.** The powder x-ray diffraction of  $\text{MnFe}_2\text{O}_4$ /bentonite composite.

composite, which could be used as adsorbents to remove a wide range of organic pollutants. Among these methods, chemical coprecipitation is the most promising because it is simple and no special chemicals and procedures are demanded (Wu, 2004; Zhang, 2007; Yang, 2008). The purpose of this work was to investigate the capability of bentonite,  $\text{MnFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$ /bentonite composite as sorbents for removal of AR138 from aqueous solution.

## MATERIALS AND METHODS

### Materials

Manganese (II) chloride and ferric chloride were obtained from Merck. Acid Red 138 (AR138-  $\text{Na}_2\text{C}_{30}\text{H}_{38}\text{N}_3\text{O}_8\text{S}_2$ ) (DiSodium 5-Acetyl Amino-3-(4-Dodcylephenyle Azo) 4-hydroxynaphtalene 2, 7 disulphide) was obtained from BDH and used without further purification. The stock solution of AR 138 1000 g/l was prepared. The diluted dye solutions prepare daily with distilled water (100 - 1000 mg/l). All reagents were of analytical grade and were used without further purification. Deionized water (18.3 MΩ) was used in all of experiments.

### Preparation of $\text{MnFe}_2\text{O}_4$ /bentonite magnetic composite

$\text{MnFe}_2\text{O}_4$ /bentonite magnetic composites were prepared using a coprecipitation method (Wu et al, 2005). 10 g of bentonite was added into a solution containing manganese (II) chloride (0.02 mol) and ferric chloride (0.04 mol) at room temperature. The pH adjusted by adding boiling NaOH (5 mol/l) solution to around 10 and stirring was continued for 30 min and then stopped. The suspension was

heated to 95 - 100°C for 2 h. After cooling, the prepared magnetic composite was repeatedly washed with distilled water. By a simple magnetic procedure, the obtained materials was separated from water and dried in an oven at 105°C for 2 h.

### The adsorption of AR138 on $\text{MnFe}_2\text{O}_4$ /bentonite

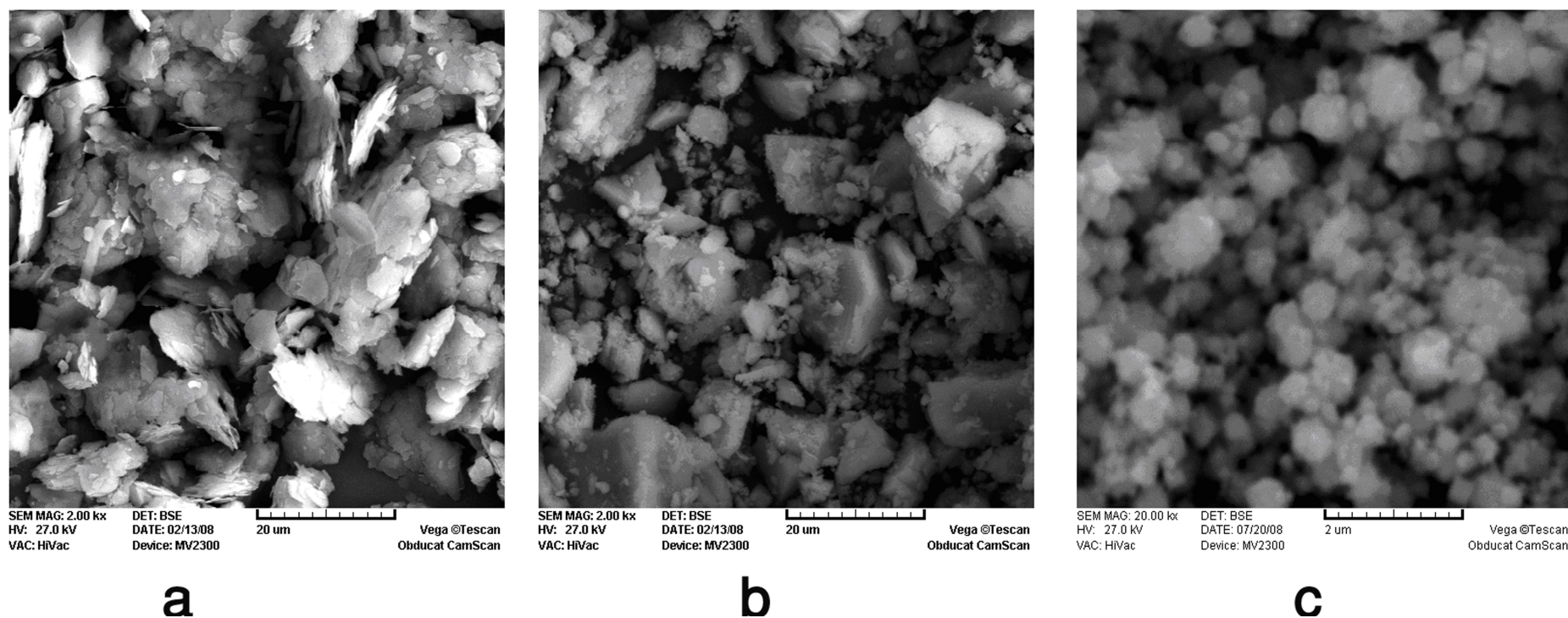
30 ml of 100 mg/l of AR 138 and 0.1 g  $\text{MnFe}_2\text{O}_4$ /bentonite were mixed and shaken in distilled water at 25°C. The mixture was filtered. The remaining AR 138 concentration in the filtrate was measured using a spectrophotometer at wavelength 515 nm.

## RESULTS AND DISCUSSION

### Characterization of composite

The chemical composition of bentonite obtained using X-ray diffraction (XRD) analysis. The XRD results indicated the presence of silica and alumina as major constituent, along with traces of sodium, potassium, iron, magnesium, calcium and titanium oxides in the form of impurities. XRD also indicated the presence of free quartz in bentonite. It is thus expected that the adsorbate species will be removed mainly by  $\text{SiO}_2$  and / or  $\text{Al}_2\text{O}_3$ . The XRD analysis indicated spinel structure of  $\text{MnFe}_2\text{O}_4$  (Figure 1).

The morphology of bentonite,  $\text{MnFe}_2\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$ /bentonite composite were studied by SEM. Figures 2a - c show the views of the natural bentonite,  $\text{MnFe}_2\text{O}_4$  magnetic ferrite and  $\text{MnFe}_2\text{O}_4$ /bentonite composite,



**Figure 2.** SEM micrographs of (a) natural bentonite, (b) pure manganese ferrite and (c) MnFe<sub>2</sub>O<sub>4</sub>/bentonite composite.

respectively. It can be observed that agglomeration of many microfine particles with diameter of about 0.3 - 0.8 µm for MnFe<sub>2</sub>O<sub>4</sub>/bentonite composite, which lead to a rough surface and the presence of a porous structure. The image also showed almost uniform nanocomposite was observed in a large scale. This conclusion was evidenced by the high surface area (350 m<sup>2</sup>/g) of the resultant nanocomposite MnFe<sub>2</sub>O<sub>4</sub>/bentonite.

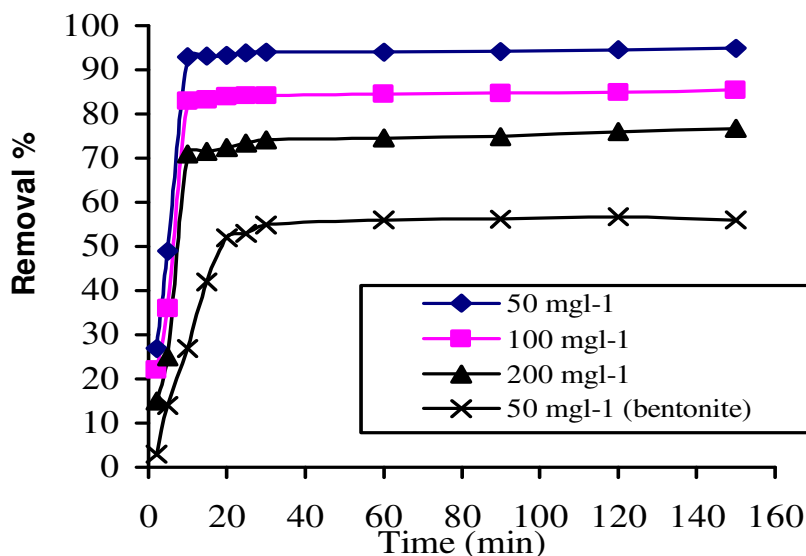
### Adsorption kinetics

The adsorption capacity of MnFe<sub>2</sub>O<sub>4</sub>/bentonite

was investigated by adsorbing acid red 138 from its aqueous solutions. The adsorption kinetic for different concentrations of AR 138 on bentonite and composite illustrated in Figure 3. The adsorption kinetic of AR 138 on the composite was very similar to that bentonite. The adsorption process could be divided into two steps, a quick step and a slow one. In the first step, the adsorption rate was fast and 92% of the equilibrium adsorption capacity was achieved within 20 min. In the subsequent step, the adsorption was slow and reached equilibrium at about 2 h. The quick adsorption may be due to the high complexation rate between the dye molecules and adsorbent and it is also related

to the fine particle size of the adsorbent. Smaller particle size (250 meshes) of bentonite and magnetic composite, were favorable for the diffusion of dye molecules onto the active sites of the sorbent. As a result, higher adsorption efficiency was realized in a shorter adsorbing time. This result indicates that the kinetic and adsorption capacity of bentonite is not affected by the presence of magnetic material and MnFe<sub>2</sub>O<sub>4</sub> had catalytic effect on dye removal (Yang, 2008).

The pseudo-first-order adsorption and the pseudo-second-order adsorption model were used to describe the kinetics of AR 138 uptake. The results are listed in Table 1. It was found, that



**Figure 3.** Kinetics of AR138 adsorption onto MnFe<sub>2</sub>O<sub>4</sub>/ bentonite composites for 0.100 g adsorbent.

**Table 1.** Kinetic parameters for AR 138 adsorption onto the MnFe<sub>2</sub>O<sub>4</sub>/ bentonite.

Pseudo-first-order			Pseudo-second-order		
A <sub>e</sub> (mg g <sup>-1</sup> )	k <sub>1</sub> (min <sup>-1</sup> )	r <sup>2</sup>	A <sub>e</sub> (mg g <sup>-1</sup> )	k <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )	r <sup>2</sup>
21.4	4.81 × 10 <sup>1</sup>	0.942	23.5	1.42 × 10 <sup>3</sup>	0.9958

the pseudo-second-order model was better capable to describe the adsorption and this suggests that the overall rate of the dye adsorption process appeared to be controlled by the chemical.

### Effect of pH on AR 138 adsorption

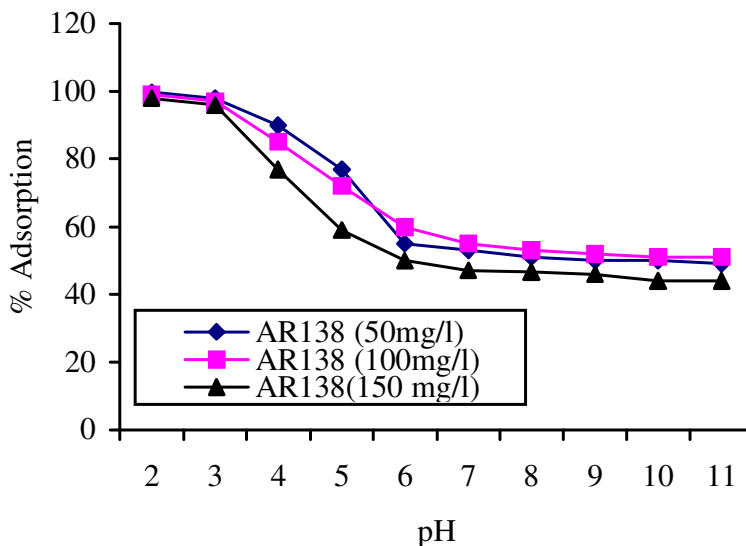
Figure 4 shows the effect of adsorption of AR 138 on MnFe<sub>2</sub>O<sub>4</sub>/ bentonite nanocomposite as a function of solution pH, using 50 ml of 50, 100 and 150 mg/l of AR 138. The adsorption of AR 138 onto MnFe<sub>2</sub>O<sub>4</sub>/ bentonite powder was strongly pH dependent. Adsorption increase drastically when the pH value was below 5. Though the reduction of AR 138 removal is relatively marked when the pH value is below 5, the AR 138 removal rate is still closely 50% at equilibrium pH around 11. This indicated that the bentonite in the composite is mainly responsible for the AR 138 removal. Therefore, the prepared composite can be used over abroad pH range. It looks, the solution pH could affect the adsorption through affecting the surface complexation reactions and the electrostatic interactions between AR138 and sorbent. In the reaction of adsorption, the charges of adsorbents and adsorbate play an important role. The heterocharge between the adsorbent and adsorbate is in favor of adsorbing reaction. From literature, a *pKa*<sub>1</sub> value of 1 for the SO<sub>3</sub>H

group and a *pKa*<sub>2</sub> value of 11.4 for the naphthalene –OH of ARB (Wu, 2005), an azo-dye with similar structure AR138, it could be deduced that at pH range studied and most of AR138 were negatively charged. On the other hand, at lower pH, more protons were available to protonate surfaces of adsorbents, which led to positive charges of adsorbent surface, thereby increased electrostatic attractions between dye molecules and surfaces of adsorbents and favored the adsorption reaction.

### Conclusions

MnFe<sub>2</sub>O<sub>4</sub>/ bentonite magnetic adsorbents with a high adsorption capacity and perfect magnetic separation performance were successfully prepared by a chemical coprecipitation method. The magnetic phase formed in the composites is spinel MnFe<sub>2</sub>O<sub>4</sub>. The composites showed high adsorption capacity for AR138. The manganese ferrite present on the surface of bentonite plays an important role in catalytic degradation of AR138 on the composite.

The adsorption kinetic data can be described by the second-order kinetic models. The adsorption capacity is related to the pH of the solution and pH 2 is optimal. It is expected that the obtained MnFe<sub>2</sub>O<sub>4</sub>/ bentonite magnetic composite can be used as potential sorbents for the



**Figure 4.** Percentage sorption of acid red 138 by MnFe<sub>2</sub>O<sub>4</sub>/bentonite at different pH (0.10 g of MnFe<sub>2</sub>O<sub>4</sub>/bentonite in 50 ml of AR 138, 30 min agitation time, 25°C).

removal of various toxic pollutants from wastewater.

#### REFERENCES

- Garg VK (2005). Removal of a basic dye from aqueous solution by adsorption using timber industry waste. *Chem. Biochem. Eng.* 19(1): 75-80.
- Garg VK (2008). Removal of Nickel (II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. *Bioresour. Technol.* 99: 1325-1331.
- Hashemian S (2007). Study of adsorption of acid dye from aqueous solutions using bentonite, *Main Group Chem.* 6(2): 97-107.
- Hashemian S (2008). African J of Biotechnol, sorption of AR138 from aqueous solutions onto rice bran, 7(5): 600-605.
- Hashemian S (2009). Modified Sawdust for removal of methyl violet from aqueous solutions. *Asian J. Chem.* 21(4): 3622-3630.
- Ho YS (2004). Kinetic modeling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp. biomass. *Bioresour. Technol.* 91(3): 249-257.
- Kavitha D, Namasivayam C (2007). Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. *Bioresour. Technol.* 98(1): 14-21.
- Khenifi A (2007). Adsorption study of an industrial dye by an organic clay, *Adsorption*, 13(2): 149-158.
- Namasivayam C (2001). Waste Manage, Removal of Cr (VI) from waste and wastewater using surfactant modified coconut, 21: 381-387.
- Oliveira LCA (2003). Clay-iron oxide magnetic composites for the adsorption of contaminants in water. *Appl. Clay Sci.* 22: 169-177.
- Robinson T (2002). Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. *Environ. Int.* 28: 29-33.
- Sud D (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions-A review, *Bioresour. Technol.* 99(14): 6017-6027.
- Wu R (2004). Removal of azo-dye acid red B (ARB) by adsorption and catalytic combustion using magnetic CuFe<sub>2</sub>O<sub>4</sub> powder. *Appl. Catal. B: Environ.* 48: 49-56.
- Wu R, Qu J (2005). Removal of water-soluble azo dye by the magnetic material MnFe<sub>2</sub>O<sub>4</sub>, *J. Chem. Technol. Biotechnol.* 27: 20-27.
- Wu R, Qu J, Chen Y (2005). Magnetic powder MnO-Fe<sub>2</sub>O<sub>3</sub> composite- A novel material of azo-dye from water. *Water Res.* 39: 630-638
- Yang N (2008). Anatase TiO<sub>2</sub> nanolayer coating on cobalt ferrite nanoparticles for magnetic photo catalyst. *Mat. Lett.* 62: 645-647.
- Zhang G (2007). CuFe<sub>2</sub>O<sub>4</sub>/activated carbon composite: A novel magnetic adsorbent for the removal of acid orange II and catalytic regeneration. *Chemosphere*, 68: 1058-1066.