Photo-catalytic response of zinc-doped nickel ferrite nanoparticles for removal of chromium from industrial wastewater

M Shoaib-ur-Rehman, Z Javaid, I Asghar, M Azam, S Shukrullah*, F Iqbal, A Maqsood and M Y Naz
Department of Physics, University of Agriculture Faisalabad, 38040 Faisalabad, Pakistan.

*E-mail: zshukrullah@gmail.com

Abstract. In this study, Ni-ZnFe$_2$O$_4$ nanoparticles were synthesized by co-precipitation technique and used to remove the chromium (Cr) metal from the industrial wastewater. The synthesized nanoparticles were characterized for their structural properties and morphology by using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The average particle size of synthesized nanoparticles was calculated by applying the Scherrer’s formula on the characteristic peaks of XRD patterns. The large surface area, controlled size and well-defined structure of the synthesized Ni-ZnFe$_2$O$_4$ nanoparticles showed remarkable results for wastewater treatment. The characterized nanoparticles were distributed into the industrial wastewater under constant stirring for 20 minutes. The nanoparticles’ suspension was subjected to UV–VIS spectrophotometry for the study of photo-catalytic behaviour of Ni-ZnFe$_2$O$_4$ nanoparticles. The effect of Ni-ZnFe$_2$O$_4$ was investigated under visible light irradiation. Zn doping in Ni-ZnFe$_2$O$_4$ showed remarkable effect on efficiency of Cr removal from the wastewater.

1. Introduction
Environmental pollution caused by industrial wastewater containing different chemicals especially synthetic dyes has become an area of special interest for scientists. Some of the industrial chemicals and synthetic dyes decompose aerobically and anaerobically resulting in the formation of carcinogenic compounds [1]. The classical techniques which were used in practice to decontaminate polluted water include adsorption, chlorination, and membrane process [2, 3]. In the past few decades, there has been great interest among scientists in developing different techniques with great prospective for environment protection applications such as water disinfection [4]. Photo-catalysts has been used successfully for the treatment of hazardous materials such as industrial effluents containing dyes. The ferrites are liked by scientists due to the properties which can be modified according to the need. The size and shape of nanoparticles are very important for adsorption process [5].

The method of adsorption with magnetic separation has been widely used in cleaning the harmful materials in the water which cause problem to human health as well as environment. Different ferrites have been used to separate different substances dissolved in the water which are not suitable [6].

Chromium is the most prior heavy metal pollutant which introduces in the human bodies from various industrials processes such as electroplating, tanning, processing of metals, fabrication of steel, paint manufacturing and photography. Chromium is mostly used in the ceramics, explosives and photography
[7]. Industries using chromium often discharge contaminated wastewater that may endanger human life and health. Chromium is a mutagenic and carcinogenic nature the presence of chromium in water is one of the most important issues.

This paper reports the efficiency of Ni-Zn ferrite nanoparticles in removing chromium from dye industrial wastewater. The adsorption technique and photo-catalytic behavior of Ni-ZnFe₂O₄ nanoparticles were investigated under visible light irradiation. UV-visible spectrometer was used to study the concentration of chromium in the solution. It was observed that chromium removal efficiency was increased with increasing of zinc doping.

2. Materials and methods

The Ni₁₋ₓZnₓFe₂O₄ with the selected “x” as 0.25, 0.50, 0.75, was prepared by co-precipitation method. In the co-precipitation method, calculated amounts of hexa-hydrated nickel chloride (NiCl₂.6H₂O), hexa-hydrated ferric chloride (FeCl₃.6H₂O), Zinc Chloride (ZnCl₂), sodium hydroxide (NaOH) and acetone (CH₃COCH₃) were weighted accurately and dissolved in doubly distilled water. The precipitation was carried out at a controlled pH of 12-13 using NaOH solution by constant stirring for 120 minutes. The beaker containing the dark brown precipitates was placed into pre-heated water bath containing water. The temperature of water bath was kept constantly at 75 °C for 2 hours for preparation of each samples. The precipitates were filtered and washed thoroughly with distilled water to make them free from sodium and chloride ions. This process continues until the pH of the residual solution reached 7.0. The final product was dried in an electric oven at heating temperature of 70 °C for 4 hours to remove the moisture contents. The fully dried samples were grinded to obtain the desired particle size. Before grinding the samples, pestle and mortar were washed carefully with acetone (CH₃COCH₃). Thereafter, the grinded precursor was annealed at 800 °C for 2 hours. The calcined samples were set to cool slowly under ambient temperature conditions.

The ferrite phases were identified through X-ray diffraction (XRD) analysis and the morphology of the prepared ferrites was examined using scanning electron microscopy (SEM). Particle size of the ferrite samples was determined using Scherrer’s formula.

The photocatalytic activity of the prepared Ni₁₋ₓZnₓFe₂O₄ ferrite samples was evaluated by absorption of Cr from dye industry under visible light irradiation. Quantity of samples S-1, S-2 and S-3 under visible light irradiation 0.05, 0.1, 0.15 and 0.20 of ferrite nanoparticles was added to 20 ml dye industry water. The solution was exposed to visible light under stirring for 20 minutes after addition of ferrite in dye water. At a given time interval, dye water was centrifuged to remove the Cr. The concentration of the Cr in solution was determined by using UV-Vis spectrophotometer.

3. Results and discussion

A typical XRD pattern of Ni₁₋ₓZnₓFe₂O₄ powder, prepared using co-precipitation method, is shown in Figure 1. This pattern confirms the formation of ferrite phases in the identified crystalline structures. The diffraction peaks also confirmed the good crystallization of the product. Sharp diffraction peaks, consistent with face centered cubic spinel structure, were noticed in XRD patterns of all the investigated samples. Peaks at 2θ of 31.9334, 34.6246, 35.6042, 36.4199 and 62.7154 were referred to XRD diffraction planes (220), (311), (311), (222) and (440) respectively. These peaks confirmed the formation of cubic spinel nickel copper ferrite when compared with JCPDS card 070-2674.

The lattice constant of Ni₁₋ₓZnₓFe₂O₄ ferrites was calculated using d-values, obtained from figure 1, in the following equation [8].

\[ d = \frac{a}{(h^2 + k^2 + l^2)^{0.5}} \]  

The lattice constant calculated for the cubic spinel structures is given in table 1. It is observed that the values of lattice constant for S-1, S-2 and S-3 are 8.36 Å, 8.35 Å and 8.33 Å, respectively. Lattice constant of Ni₁₋ₓZnₓFe₂O₄ was not significantly influenced by a change in concentration. Negligible effect of different concentrations on the lattice constant was noted in the presented work. The lattice
constant values were in a close agreement with the results published by the American Society for Testing Materials [9].

**Figure 1.** Typical XRD patterns of co-precipitated S-1 sample of Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$.

**Table 1.** Estimated amount of Zn in Ni-Zn ferrite nanoparticles for the removal of Cr from industrial wastewater.

| Zn Con. (g/l) | Stirring time (min) | Cr in untreated samples (g/l) | Amount of Cr in treated samples (g/l) |
|--------------|---------------------|------------------------------|---------------------------------------|
| S-1          | S-2                 | S-3                          |
| 0.05         | 20                  | 0.65                         | 0.42 0.40 0.36                         |
| 0.10         | 20                  | 0.65                         | 0.40 0.30 0.30                         |
| 0.15         | 20                  | 0.65                         | 0.32 0.36 0.30                         |
| 0.20         | 20                  | 0.65                         | 0.30 0.35 0.26                         |

The volume of the unit cell of the synthesized samples was calculated using the respective lattice constant values from Table 1. The relation between the volume and the lattice constant exists in the form:

$$V = a^3$$

The calculated volume of the samples is also given in Table 2. It can be observed that the values of volume of the unit cell for S-1, S-2 and S-3 are 584.28 Å, 582.18 Å and 578.01 Å, respectively. Negligible effect of concentration on volume of the unit cell of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ was seen due to negligible variation in lattice constants.

The crystal size of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrite samples was determined by considering the most intense diffraction peaks (311) in XRD patterns. In this study, the Debye-Scherrer formula was used to calculate the crystal size of tested samples as shown by equation (3):

$$T = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where ‘$\theta$’ is the Bragg angle between incident ray and diffracted plane, ‘$\lambda$’ is the wavelength of X-rays used and ‘$\beta$’ is measured in radians (line broadening at intensity equal to the half maximum intensity). Table 2 shows that crystal size for S-1 (Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$), S-2 (Ni$_{0.50}$Zn$_{0.50}$Fe$_2$O$_4$) and S-3
(Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$) calcinated at same temperature of 800 °C, are 51.56 nm, 39.92 nm and 33.01 nm, respectively. It has been found that the crystal size decreases with a decrease in the concentration of Ni$_{1-x}$Zn$_{x}$Fe$_2$O$_4$ and increases with an increase in the ferrite concentration. The average crystal size decreases with the decreasing Ni content in Ni$_{1-x}$Zn$_{x}$Fe$_2$O$_4$ nanoparticles. It may be due to small grain growth of Ni (Mote et al., 2013). Besides that, the crystal size increases with an increase in calcinating temperatures [10].

Table 2. Lattice constant $a$, volume $V$, crystalline size $T$ and x-ray density of Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$ calcinated at 800 °C.

| Sample Name | $a$ (Å) | Volume | $T$ (nm) | $d$ (gm/cm$^3$) |
|-------------|---------|--------|----------|----------------|
| S-1         | 8.36    | 584.28 | 51.56    | 5.36           |
| S-2         | 8.35    | 582.18 | 39.92    | 5.43           |
| S-3         | 8.33    | 578.01 | 33.01    | 5.41           |

The SEM images for Ni$_{1-x}$Zn$_{x}$Fe$_2$O$_4$ ($x = 0.25, 0.50$ and $0.75$) shown in figure 2. The grain sizes of S-1 and S-3 are same as 0.2 while S-2 is 0.1 μm. SEM graph of the synthesized samples shows their morphology. The graphs were obtained using secondary electron detector such as semi-inlens. Meanwhile, the images were obtained with the semi-inlens secondary electron detector. SIMS depth profiles were made using a ToF-SIMS 5 (IONTOF GmbH, Munster, Germany). Depth profiles of all the samples were carried out in the non-interlaced mode with instrument JSM-5910 at accelerated voltage of 20 volt.

Figure 2. SEM micrographs of (a) S-1 (Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$) (b) S-2 (Ni$_{0.50}$Zn$_{0.50}$Fe$_2$O$_4$) and (c) S-3 (Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$).

The photoluminescence spectra was recorded for the study of optical properties and the recombination of energetic position of sub band gap defects states and photo generated charge carriers. Figure 3 shows the spectra of Ni$_{1-x}$Zn$_{x}$Fe$_2$O$_4$ nanoparticles at excited wavelength of 430 nm. In this work,
the emission peaks in the UV range at 371–493 nm results from the recombination of excited electron and holes. The emissions peaks between 415–450 nm correspond to the violet emission which might be due to the presence of lattice defects, oxygen vacancies and grain boundaries in Ni_{1-x}Zn_xFe_2O_4 nanoparticles [10]. The lowering of luminescence intensity of ferrites with increase in doping fraction, leads to the decrease in recombination rate of electrons-holes under light irradiation and the higher separation rate of photo generated electron-hole pairs efficiently.

![Figure 3. Photoluminescence spectra of S-1 (Ni_{0.75}Zn_{0.25}Fe_2O_4), S-2 (Ni_{0.5}Zn_{0.5}Fe_2O_4) and S-3 (Ni_{0.25}Zn_{0.75}Fe_2O_4).](image)

Irradiation of industrial wastewater in the presence of Ni_{1-x}Zn_xFe_2O_4 (x= 0.25, 0.50 and 0.75) nanoparticles with two units of 200 Watt Hg lamp lead to a change in absorbance with 20 minutes time. Photocatalytic activity of NiZn Fe_2O_4 on dye industrial wastewater with different concentration of Zn is given in table 3. It was observed that the removal efficiency increases as the Zn concentration increase.

| Sample Name | Concentration | Calcinated Temp. (°C) | Removal Efficiency (%) |
|-------------|---------------|-----------------------|------------------------|
| S-1         | 0.25          | 800                   | 40.22                  |
| S-2         | 0.50          | 800                   | 48.18                  |
| S-3         | 0.75          | 800                   | 60.09                  |

It can be observed that for all three samples the highest removal efficiency from wastewater is obtained in 20 minutes of stirring. At higher stirring time, the increasing of the adsorption process efficiency is not significant. Therefore, it is not recommended to work under higher stirring time from the economic point of view.

4. Conclusion
The well single cubic structures of Ni_{0.75}Zn_{0.25}Fe_2O_4, Ni_{0.5}Zn_{0.5}Fe_2O_4 and Ni_{0.25}Zn_{0.75}Fe_2O_4 phases were synthesized and calcining all samples at 800 °C for 2 hours. The XRD patterns of co-precipitated samples showed the (3 1 1) peak at 2θ=35. With an increase in concentration of zinc in Ni_{1-x}Zn_xFe_2O_4 ferrite nanoparticles, the crystal size was decreased. The ranges of lattice constant for all the three samples are 8.36Å, 8.35Å and 8.33Å. The average crystal size for all the three samples of Ni_{1-x}Zn_xFe_2O_4 was remained in the range of 51.56 nm to 33.01 nm. The x-ray density of the samples increases with the increase in concentration of zinc. It was observed that for all three samples, the highest removal efficiency of the Cr from the wastewater was possible during the first 20 minutes of stirring and S-3 is found to be most effective among all other sample for Cr removal. At higher stirring times, the adsorption efficiency was not significantly by the time.
References
[1] Afkhami A, Sayari S, Moosavi R and Madrakian T 2015 J. Ind. Eng. Chem. 21 920.
[2] Ali I 2012 Chem. Rev. 112 5073.
[3] Chandamma N, Manohara B M, Ujjinappa B S, Shankarmurthy G J and Kumar M S 2017 J. Alloy. Compd. 702 479.
[4] Cheng Z, Tan A L K, Tao Y, Shan D, Ting K E and Yin X J 2012 Int. J. Photoenergy 69 1.
[5] Duan Q, Lee J, Chen H and Zheng Y 2017 Water Sci. Technol. 76 3069.
[6] Erdem M and Tumen F 2004 J. hazard. Mater. B 109 71.
[7] Fang B, Yan Y, Yang Y, Wang F, Chu Z, Sun X, Li J and Wang L 2016 Water Sci. Technol. 5 1112.
[8] Toqeer I, Naz M Y, Khan Y, Azam M, Alkanhal M A S Meer R M M 2019 Philos. Mag. Lett. 99 67.
[9] Ge F, Zhu L and Wang J 2008 Desalination 225 156.
[10] Gul I H, Abbasi A Z, Amina F, Anis-ur-Rehman M and Maqsood A 2007 J. Magn. Magn. Mater. 311 494.
[11] Gul I H, Ahmed W and Maqsood A 2008 J. Magn. Magn. Mater. 320 270.