CHARACTERIZATION AND APPLICATION OF MAGNETITE AND GOETHITE FOR WASTEWATER TREATMENT

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Abstract

In this research work, two different types of iron oxides (magnetite and goethite) were synthesized by co-precipitation method. These iron oxides were characterized by using some modern techniques (XRD, SEM, EDXRF and FT IR). According to XRD data, eight Miller indices [(111), (220), (311), (222), (400), (422), (511), (440)] of the magnetite samples were found. Three Miller indices [(130), (110), (200)] of the goethite sample were observed. SEM micrograph of magnetite and goethite samples indicated the porous nature of iron oxide samples. According to EDXRF data, the prepared iron oxides showed the presence of iron (100 %) and no other elements were present. According to FT IR data, the magnetite and goethite samples showed the presence of iron-metal oxide bonds. The bands at 894.9 cm^{-1} be possible due to the iron oxide for magnetite samples and the band located at 891.1 cm^{-1}may be Fe-O groups for goethite sample. Application of magnetite and goethite iron oxide samples were carried out by using model solutions for wastewater treatment. Sorption capacity on magnetite and goethite were measured for contact time and effect of dosage. The efficiency of iron oxide samples for the removal of dyes in wastewater samples were also studied.

Keywords: Magnetite, goethite, iron oxide, dyes, sorption capacity

Introduction

There is an ever-increasing world demand for fabrics due to population growth. In order to meet demand for fabrics more textile industries are being started daily. Not only the textile sector, but also other industries, use dyes and

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pigments to colour their products and to increase the market of their product (Popoola *et al.,* 1994). Other industries that discharge their wastewater into natural streams include producers of carpets, wool, and paint also the pigment paper and pulp mills, tanneries, electroplating industries, distrilleries, food companies and the printing industry (Guinot *et al.*, 2006). These industries discharge effluents bearing dyes, surfactants salts and heavy metals. Such discharge has created significant concern, as dyes impart toxicity and visibility. Dyes are almost invariably toxic and additionally a visible pollutant. So their removal from effluent stream is ecologically essential. The American Dye Manufacturing Institute showed that the basic dyes are generally more toxic than acid or direct dyes (Mathur and Bhandari, 2001).

Recent estimates indicate that approximately 12% of synthetic dyes used each year are lost during manufacture and processing operates and that 20-35% of these input dyes (Allen and Koumanova, 2005).The textile effluents composition is complex since it contains diverse dyes and other products such as dispersants, acids, alkalis, salts and some heavy metals. In general the effluent is highly colored, with a high biological (BOD) and chemistry demands of oxygen (COD) (Boyjoo, 1987).

Dyes are present in the textile effluent in concentrations of 10 to 50 mg/L. Approximately 1,000,000 kg/year of dyes are discharged in effluents by the textile industries, because approximately a 15% of the total dye used in the process is lost during the dying process. Color removal from textile effluents has been the target of great attention in the last few years, not only because of its potential toxicity, but mainly due to the potential environmental impact. Different treatments for the removal of dyes have been used such as special processes of filtration, activated mud, chemical coagulation, adsorption on activated carbon and processes of photodegradation. The solution to the problem depends on the use of different technological process.

One of the methods used to eliminate dyes of the effluents is the adsorption on a solid material. The most common adsorbent is the activated carbon, effective in the removal of organic components and not effective in the removal of inorganic compound. Due to its high cost, the use of alternative and efficient adsorbents for the removal of dyes and metals is been increasingly studied. Oxides and metal hydroxides have also been used as adsorbents in the

textile industry. The adsorption of cationic and anionic dyes on hydrated zirconium oxide or iron oxides has been reported. These materials are common as adsorbents by their limited solubility and their amphoteric properties. However, sometimes these oxides present low surface area and this aspect is a problem to resolve.

Goethite (FeO(OH)), is an iron bearing oxide mineral found in soil and other low-temperature environments. Goethite has been well known since prehistoric times for its use as a pigment. Evidence has been found of its use in paint pigment samples taken from the caves of Lascaux in France. It was first described in 1806 for occurrences in the Mesabi iron ore district of Minnesota. Recently, nanoparticulate authigenic goethite was shown to be the most common diagenetic iron hydroxide in both marine and lake sediments.

Magnetite is one of the most common oxide minerals and also one of the most common iron minerals. It is an important ore of iron and is found in igneous, metamorphic and sedimentary rocks (Forsling and Samshog, 1998). It can also be abundant in sediments. Magnetite is easy to identify. It is a black opaque, submetallic to metallic mineral with a hardness between 5.5 and 6.5. It is often found in the form of isometric crystals. However, its magnetic properties are distinctive. It is one of just a few minerals that are attracted to a work magnet. It is the most magnetic mineral found in nature. Sometimes it is automagnetized and attracts metal objects (Schwertmann and Cornell, 1964).

Materials And Methods

The following analytical grade reagents:$FeSO_4.7H_2O$,NaOH,$NaNO_3$ and $Fe(NO_3)_3.9H_2O$ were obtained from Analytical Laboratory Department of Chemistry, University of Yangon. The chemicals used in this research work were purchased from British Drug House (BDH) chemicals Ltd. Magnetite is prepared by slow adding the iron (II) sulphate solution into the beaker containing the solution of sodium nitrate and sodium hydroxide. The black precipitate was obtained and the sample was aged at room temperature for 16 days. Goethite was prepared by adding ferric nitrate in to a beaker containing sodium hydroxide solution .The precipitate obtained was aged at room temperature for 48 h and then in an oven at 65°C for 72 h.

The sample were characterized by SEM, EDXRF, FTIR and XRD. Sorption properties of these samples were determined with eriochrome blue black B and alizarin red S dyes. In the contact time effect 0.2 g of sample was placed into separated glass stoppered bottles and treated in 20 mL 20 ppm dye solution at pH 7.The bottles containing dye and iron oxide as absorbents were placed in the thermostatic shaker at room temperature. The contact time setting were 10,20,30,40,60,120 and 180 min. After shaking the sample solutions were filtered off and the filtrates were spectrophotometrically measured at maximum wavelengths. The removal percent of dyes with the iron oxides were calculated by the equation $R\,(\%) = \frac{C_0 - C_e}{C_0} \times 100$ .The dosage effect were carried out by the similar procedure.

Furthermore application of prepared iron oxide samples for the removal of dyes in wastewater sample (collected from south Dagon Myothit) were determined. In this research absorption spectrum of wastewater samples were recorded by using UV-visible spectrophotometer. In this study a 50mL of wastewater was mixed with 2.5g of magnetite powder in a bottle. The bottle was agitated in thermostatic shaker at temperature of 30 °C for 1h. Then the solution was filtered off and the absorbance of resultant filtrate was measured. The same procedure was carried out for the goethite sample.

Results and Discussion

Preparation of Magnetite and Goethite Samples

Magnetite and Goethite were prepared in the laboratory by co-precipitation method. Figures 1 and 2 show photographs of Magnetite and Goethite.

Characterization of Prepared Iron Oxide Samples (magnetite and goethite) by SEM, EDXRF, FT IR and XRD

Surface morphology of the prepared iron oxide samples

Surface morphology of the prepared iron oxide samples were studied, by using SEM. Figures 3 and 4 show the SEM micrographs of magnetite and goethite samples respectively. The SEM microphotographs indicated the porous nature of the surface. Therefore dyes can enter the porous of the iron oxide samples.

EDXRF data of the prepared iron oxide samples

EDXRF measurements were carried out on prepared iron oxide samples. Figures 5 and 6 show the EDXRF spectra of magnetite and goethite samples respectively. According to the EDXRF data the prepared iron oxide samples were pure and free from impurities.100% of iron are present in these samples.

FTIR data of the prepared iron oxide samples

FT IR measurements were carried out on the prepared iron oxide samples. Figures 7 and 8 show the FT IR spectra of prepared iron oxides. FT IR data indicated the presence of functional groups in the samples. Tables1 and 2 showed the FT IR data of magnetite and goethite samples. In the magnetite sample O-H stretching vibration was found at 3448.5cm^{-1}, O-H in plane bending vibration was found at 1357.8 cm^{-1} and Fe-O group vibration was found at 894.9cm^{-1}.In the goethite sample O-H stretching vibration was found at 3132.2cm^{-1},O-H in plane bending vibration was found at 1380.9cm^{-1} and Fe-O group vibration was found at 891.1cm^{-1} respectively.

X**RD Data of the Prepared Iron Oxide Sample**

XRD measurements were carried out on the prepared iron oxide samples. Figures 9 and 10 depicted the XRD pattern of magnetite and goethite samples respectively.XRD pattern can be used to examine the phase purity and phase structure. The XRD pattern of magnetite sample clearly matched with the standard library data of PDF-19-0629-magnetite. Eight Miller indices [(111),(220), (311),(222), (400),(422), (511),(440)] of the magnetite sample

matched with the standard data(Fe_3O4).XRD pattern of goethite sample matched with the standard library data of PDF-81-0464-FeO(OH). Three Miller indices [(130),(111),(200)] of the goethite sample matched with the standard data.

Sorption Study of Magnetite and Goethite using Modern Dye Solutions

Effect of contact time on sorption of eriochrome blue black B

Sorption capacity of magnetite and goethite samples onto eriochrome blue black B were studied. Tables 3 and 4 described the relationship between contact time and percent of eriochrome blue black B on magnetite and goethite samples. Figure 11 show plot of eriochrome blue black B sorbed percent as a function of contact time on magnetite and goethite samples. For the contact time of 180 min 70.34 % and 77.50 % of eriochrome blue black B were sorbed on magnetite and goethite samples, respectively.

Effect of dosage on sorption of eriochrome blue black B

Effect of dosage of the prepared iron oxide samples on eriochrome blue black B dye was studied by choosing the dosage of the prepared iron oxide samples from 0.1 to 1.4 g. Tables 5 and 6 show the relationship between dosage of magnetite and goethite, respectively, with the percent sorption of eriochrome blue black B.

Figure 12depicted the histogram of percent sorption of eriochrome blue black B with dosage of the prepared iron oxide samples.By using 1.4 g of magnetite and goethite samples, sorption percent of eriochrome blue black B were 88.40 % and 89.10% respectively.

Effect of contact time on sorption of alizarin red S

Sorption capacity of magnetite and goethite samples onto alizarin red S were studied. Tables 7 and 8 shows the relationship between contact time and percent sorption of alizarin red S on magnetite and goethite samples respectively. Figure 13 shows plot of sorption percent of alizarin red S as a function of contact time on magnetite and goethite samples. For the contact

time of 180 min, sorption of alizarin red S on magnetite and goethite samples were 83.56%and 89.00% respectively.

Effect of dosage on sorption of alizarin red S

Effect of dosage of the prepared iron oxide samples on sorption of alizarin red S dye was studied by choosing the dosage of the prepared iron oxide samples from 0.1 to 1.4 g. Tables 9 and 10 show the relationship between dosage of magnetite and goethite, respectively with the percent sorption of alizarin red S.

Figure 14 shows the histogram of sorption percent of alizarin red S with dosage of the prepared iron oxide samples. By using 1.4 g of magnetite and goethite samples, sorption percent of alizarin red S were 90.25% and 90.65% respectively.

Application of iron oxide samples for the removal of dyes in wastewater samples

Applications of the prepared iron oxide samples were studied for the treatment of dyes in wastewater. Wastewater samples were collected from pulp and paper industry, South Dagon MyoThit. The wavelength of maximum absorption of wastewater sample was found to be 414.24nm. After treatment the results show that sorption percent of dye on magnetite and goethite were 87.32%, 99.41% respectively. Table 11 shows the percent removal of dyes from wastewater sample by magnetite and goethite samples. Figure 15 shows the wastewater samples after treatment with magnetite and goethite samples.

Figure 1. The photograph of prepared magnetite

Figure 2. The photograph of a prepared goethite

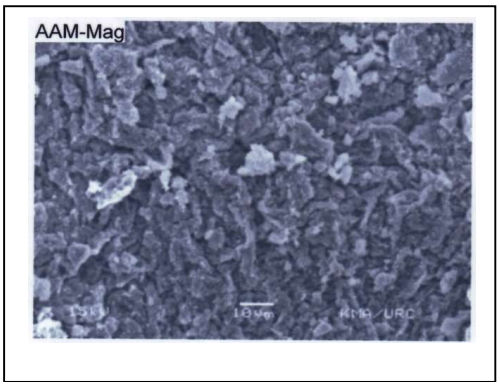

Figure 3. SEM micrograph of magnetite (X 1000)

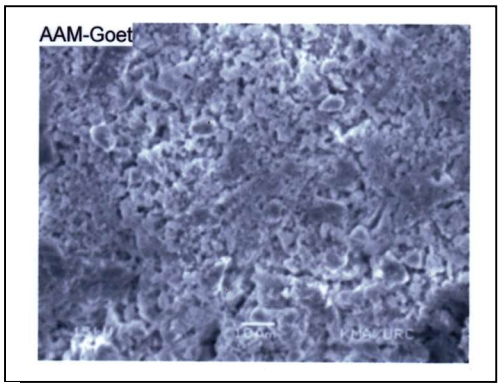

Figure 4. SEM micrograph of goethite (X 1000)

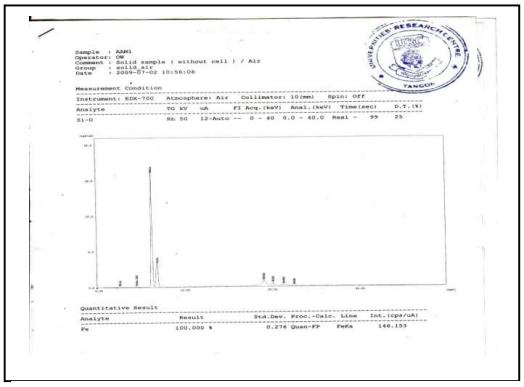

Figure 5. EDXRF spectrum of prepared magnetite

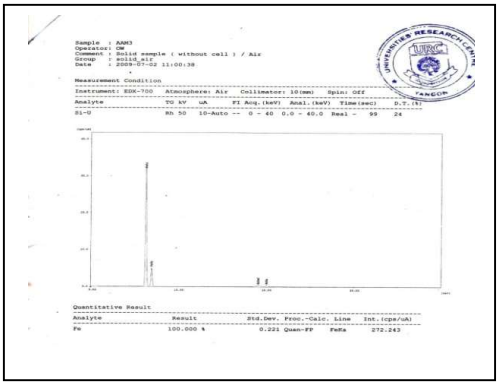

Figure 6. EDXRF spectrum of prepared goethite

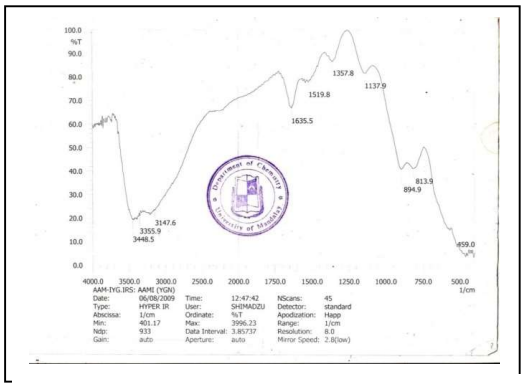

Figure 7. The FT IR spectrum of prepared magnetite sample

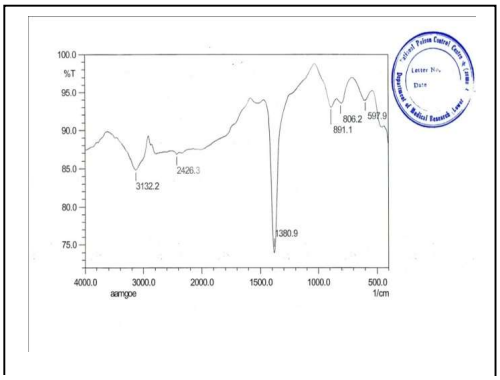

Figure 8. The FT IR spectrum of prepared goethite sample

Table 1. FT IR Data of Prepared Magnetite Sample

No.	Wave number (cm^{-1})	Functional group
1	3448.5	ν_{O-H} stretching
2	1357.8	ν_{O-H} in plane bending
3	894.9	$\nu_{Fe-O,}$Fe-O group

Table 2. FT IR Data of Prepared Goethite Sample

No.	Wave number (cm^{-1})	Functional group
1	3132.2	ν_{O-H} stretching, - OH group
2	1380.9	ν_{O-H} in plane bending, -OH group
3	891.1	$\nu_{Fe-O,}$Fe-O group

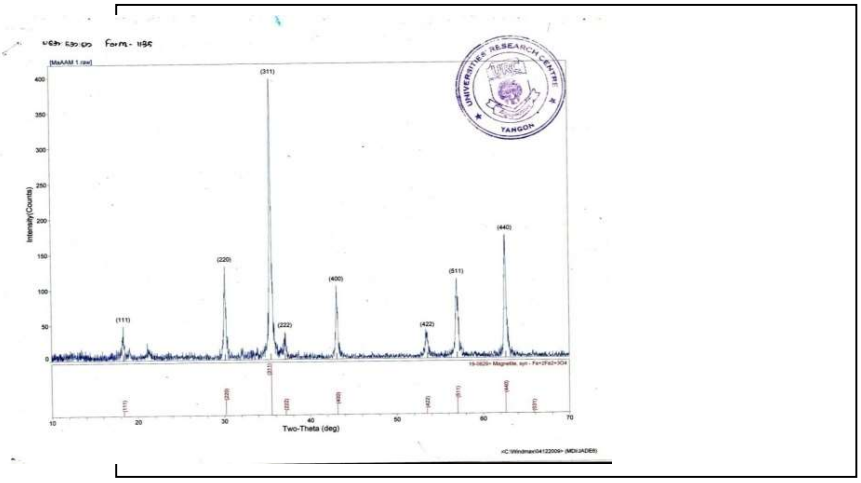

Figure 9. XRD pattern of the prepared magnetite

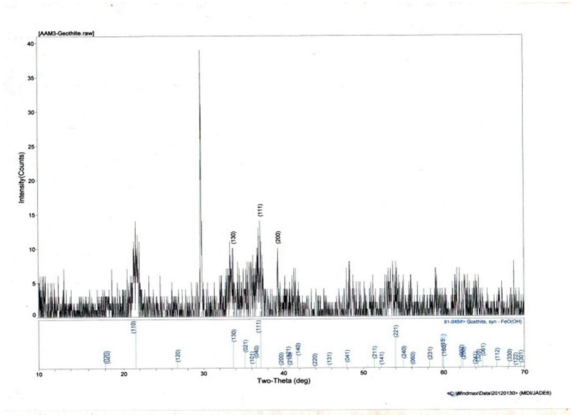

Figure 10. XRD pattern of the prepared goethite

Table 3. Relationship between Contact time and Percent Sorption of Eriochrome Blue Black B on Magnetite

Contact time (min)	**Percent sorption of EBBB (%)**
0	0
10	25.00
20	41.34
30	52.54
40	60.49
60	63.97
120	69.80
180	70.34

Experimental condition pH=7
Amount of magnetite =0.2 g
Concentration of dye = 20 ppm
Volume of EBBB solution=20mL

Table 4. Relationship between Contact Time and Percent Sorption of Eriochrome Blue Black B on Goethite

Contact time (min)	Percent sorption of EBBB (%)
0	0
10	27.95
20	33.80
30	43.40
40	53.70
60	67.65
120	77.50
180	77.50

Experimental condition
pH=7
Amount of magnetite =0.2 g
Concentration of dye = 20 ppm
Volume of EBBB solution=20mL

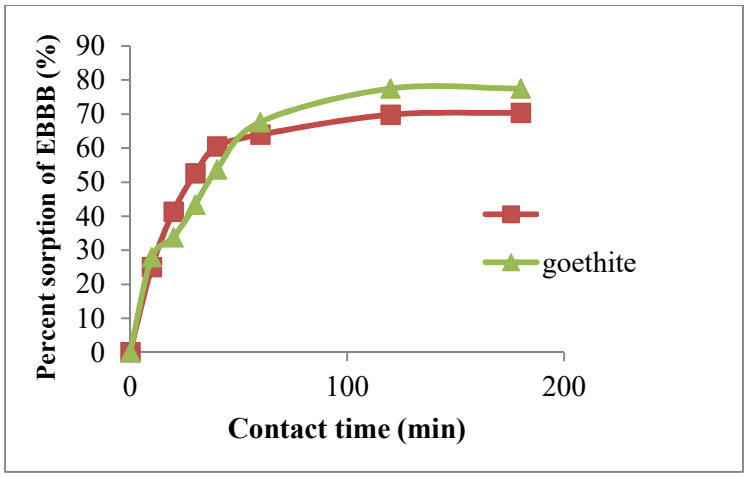

Figure 11. Plot of percent sorption of eriochrome blue black B as a function of contact time on magnetite and goethite

Table 5. Relationship between Dosage of Magnetite and Percent sorption of EBBB

Weight of Magnetite (g)	Percent sorption of EBBB (%)
0.1	33.65
0.2	63.81
0.4	73.74
0.6	77.56
1.0	85.37
1.4	88.40

Experimental condition pH=7
Concentration of dye=20 ppm
Contact time=1hr
Volume of EBBB solution=20 mL

Table 6. Relationship between Dosage of Goethite and Percent sorption of EBBB

Weight of Goethite (g)	Percent sorption of EBBB (%)
0.1	46.56
0.2	76.25
0.4	80.45
0.6	85.7
1.0	89.05
1.4	89.10

Experimental condition pH=7
Contact time =1hr
Concentration of dye=20 ppm
Volume of EBBB solution=20mL

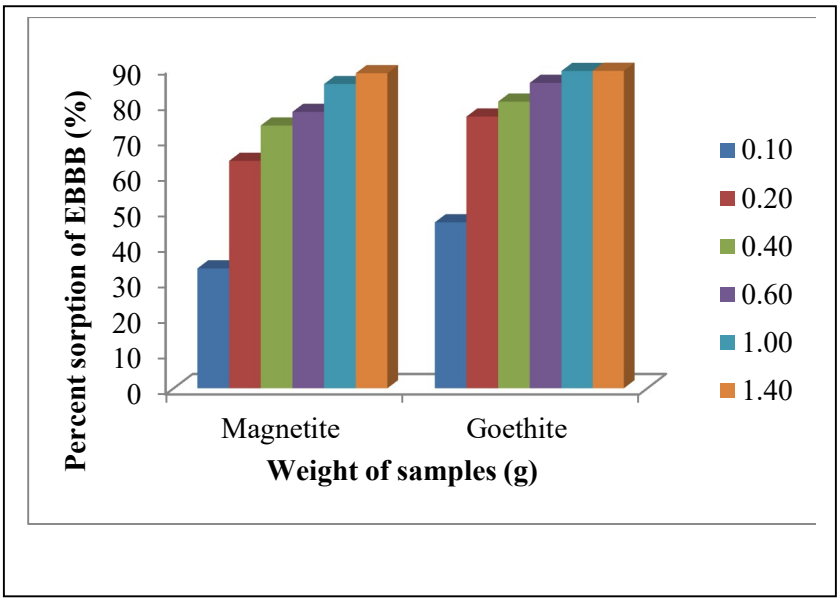

Figure 12. Histogram of percent sorption of EBBB with dosage of the prepared iron oxide samples

Table 7. Relationship between Contact Time and Percent sorption of Alizarin red S on Magnetite

contact time(min)	Percent sorption of Alizarin red S (%)
10	28.75
20	34.25
30	52.05
40	64.35
60	78.08
120	82.19
180	83.56

Experimental condition
pH=7
Concentration of dye=20 ppm
Amount of magnetite=0.2g
Volume of alizarin red S solution=20 mL

Table 8. Relationship between Contact Time and Percent sorption of Alizarin red S on Goethite

Contact time(min)	Percent sorption of Alizarin red S (%)
10	33.05
20	45.25
30	60.05
40	79.35
60	88.95
120	89.00
180	89.00

Experimental condition pH=7
Concentration of dye = 20 ppm
Amount of Goethite = 0.2 g
Volume of alizarin red S solution = 20 mL

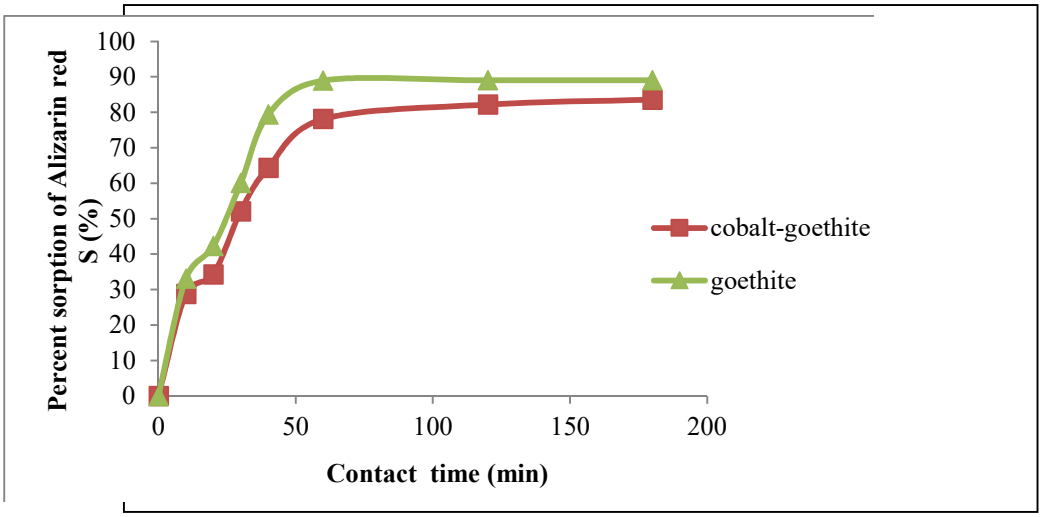

Figure 13. Plot of sorption percent of alizarin red S as a function of contact time on magnetite and goethite

Table 9. Relationship between Dosage of Magnetite and Percent Sorption of Alizarin red S

Weight of Magnetite (g)	Percent sorption of Alizarin red S (%)
0.1	48.45
0.2	76.25
0.4	83.55
0.6	88.85
1.0	89.75
1.4	90.25

Experimental condition pH=7
Contact time=1 h
Concentration of dye=20 ppm
Volume of alizarin red S solution=20 mL

Table 10. Relationship between Dosage of Goethite and Percent Sorption of Alizarin red S

Weight of Goethite (g)	Percent sorption of Alizarin red S (%)
0.1	56.45
0.2	89.00
0.4	90.05
0.6	90.10
1.0	90.60
1.4	90.65

Experimental condition pH=7
Contact time = 1 h
Concentration of dye = 20 ppm
Volume of alizarin red S solution = 20 mL

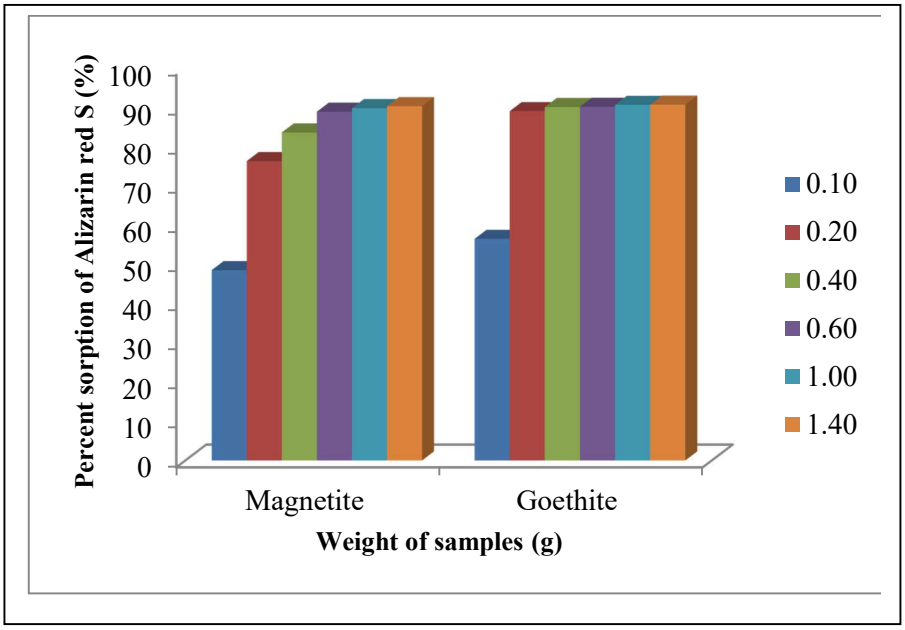

Figure 14. Histogram of percent sorption of alizarin red S with dosage of the prepared iron oxide samples

Table 11. Treatment of Wastewater Samples by the Prepared Iron Oxides

Iron Oxide Sample	Dye removal %
Magnetite	87.32
Goethite	99.41

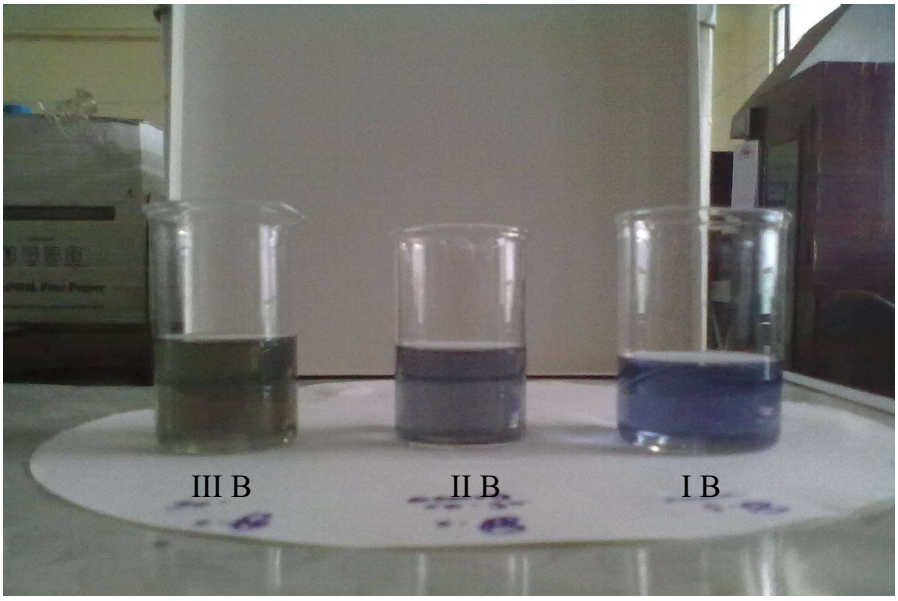

Figure 15. Photograph of wastewater sample

I B = Sample before treatment
II B = Sample after treatment with goethite
III B = Sample after treatment with magnetite

Conclusion

In this research, iron oxides were synthesized by co-precipitation method. Characterization of the prepared iron oxides were carried out by using SEM, EDXRF, FT IR and XRD. The SEM micrographs indicated the porous nature of the surface. Therefore dyes can enter the pores of iron oxide samples. From EDXRF patterns it was found that the prepared magnetite and goethite were pure and free from impurities. The FT IR data of magnetite and goethite showed the presence of Fe-OH and Fe-O groups. The XRD diffractogram of the magnetite sample well matched with the standard XRD data of Fe_3O_4 and goethite well matched with the standard XRD data of FeO(OH) in software library. Sorption properties of goethite is a little higher than that of magnetite,

this is because the formula of goethite is FeO(OH), magnetite is Fe_3O_4. OH groups in the goethite have strong attractive interaction with functional groups in the dyes. From the wastewater treatment it can be seen clearly that colours of wastewater decreased significantly after treatment. According to the results, it can be concluded that the prepared iron oxides (magnetite and goethite) can be used effectively for the removal of dyes from wastewater.

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