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Effective Adsorption of Eriochrome Black T From aqueous Solution using γ -Fe_2O_3 nanopowder

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Abstract:

In this study, nano sized γ-Fe_2O_3 powder was prepared by low temperature combustion method and used as an effective adsorbent for the removal of toxic azo dye, Eriochrome Black T from aqueous solution. The powder was characterized by powder X-ray diffraction (PXRD), Scanning electron microscopy (SEM), Fourier transform infrared spectra (FTIR). The XRD results reveals the formation of well crystalline Fe_2O_3 in hexagonal phase along with small Fe_3O_4 impurity peaks. The adsorption studies were carried on 10 ppm dye solution at different parameters like Initial dye concentration, adsorbent dosage and contact time. The experimental result shows that, the maximum percentage adsorption (70%) is observed at 40 mg of γ -Fe_2O_3 nano powder, at contact time of 8 min.

Keywords: solution combustion, PXRD, FTIR, SEM, Adsorption, waste water

1. Introduction

A dye is a natural or synthetic substance used to add a color or to change a color of a substance. The dyes have a wide range of industrial application such as textiles, painting, leather, printing, photography coating, cosmetics, pharmaceuticals and photochemical industries, these organic dyes seriously induce water pollution and even they are carcinogenic [1-3]. Moreover, they are very stable to light, temperature, and microbial attack, making them recalcitrant compounds [2]. Dyes are basically in colored, ionizing and aromatic organic compounds which show an affinity towards the substrate to which it is being applied [3]. It is commonly applied as a aqueous or oil based solution. The general classification of dyes evolved based on the chromophoric group in the molecular moiety as acridine dyes, azo dyes, metal complex dyes, anthraquinone dyes, nitro dyes, dispersed based dyes, xanthene dyes and quinine-amine dyes, etc [3,6]. Discharge of these synthetic dyes into aqueous bodies as posed a serious threat to human being and aquatic life [3]. These carcinogenic dyes also damage the water esthetic by obstructing light penetration which decreases the photosynthesis in aquatic plants and raises the chemical oxygen demand (COD). It can cause allergic dermatitis, skin irritation, cancer and mutation [4].

There are several physical, chemical and biological methods are employed for the removal of these carcinogenic dyes, they are chemical oxidation, ozonation, membrane filtration, biological treatment, coagulation, adsorption and biosorption have been reported extensively [2-4]. Few of these processes are effective when concentration of dye in the effluent are in small traces, some of them causing large quantity of sludge causing disposal problems, which increases the operational cost. Advanced Oxidation Processes (AOPs) involve the generation of highly reactive hydroxyl radicals which have one unpaired electron and are very strong oxidizing agents. Fenton Process suffer from a drawback that it requires the removal of iron ions present in the sludge which is expensive and requires large amount of chemical and man power [5]. In recent years among many methods, adsorption technique for wastewater treatment have been widely accepted and practiced by researchers. However, adsorption has advantages over other methods because of its lower land area requirement, constancy and easy implementation, adsorbent surface area, more active sites for interaction with the adsorbate and mainly dosage requirement is very less. Selection of suitable adsorbent and operating conditions in adsorption process is the key and challenging aspect to achieve maximum removal of the pollutants [1, 7, 8].

In the present investigation, γ-Fe_2O_3 nano sized powder have been used for removal of Eriochrome Black T, which is also used as an indicator in complexometric titrations for determination of metallic ions and for biological staining. However, this dye is hazardous as such as its degradation products like napthaquinone are still more carcinogenic nature [7]. A literature survey showed that only few papers have raised the removal of EBT [7-11]. Therefore, we adopted γ-Fe_2O_3 nano powder as an efficient adsorbent for removal of azo dye from aqueous solution.

2. Experimental Methods

2.1 Materials and Methods

All the chemicals and reagents used in this study were of analytical grade. Commercially pure ferric nitrate nitrate $Fe(NO_3)_3 \cdot 9H_2O$,99% Merck), glycine (NH_2, CH_2COOH 99% Merck).

2.2. Instruments

Prepared γ-Fe_2O_3 nano powder analysis was carried out using XRD model Philips X-Ray diffractometer (PW/1050/70/76) with CuK_α radiation (λ = 1.54Ǻ) at room temperature. The morphology of powders was examined using JEOL (JSM-840A) scanning electron microscopy (SEM). FTIR spectra were recorded using Nicollet IMPACT 400 D FTIR spectrometer, in the range 400–4000 cm^{-1} as KBr pellet. The absorption spectra were recorded with a UV-visible spectrophotometer (Elico-159).

2.3 Preparation of γ-Fe_2O_3 nano powder.

An aqueous solution containing stoichiometric amounts of ferric nitrate and glycine were taken in a ceramic dish of approximately 150 ml capacity. The excess water was evaporated by heating over a hot plate. The ceramic dish was introduced into a muffle furnace maintained at about 400 ±10 ^{0}C. The reaction mixture undergoes combustion liberating gaseous products such as oxides of nitrogen and carbon. The chemistry of the redox reaction between the metal nitrate and the fuel follows the stoichiometry of the following reaction:

$2Fe(NO_3)_3 + 2NH_2CH_2COOH \rightarrow Fe_2O_3\ (s) + 4CO_2\ (g) + 5H_2O\ (g) + 4N_2$ -----------(1)

2.3 Preparation 10 ppm EBT solution

In this investigation Eriochrome Black T is used as a model dye for its removal form aqueous medium. It is majorly used for dying silk, wool, nylon multifiber after pretreatment with chromium salts. Pure EBT [$C_{20}H_{12}N_3O_7NaS$] whose IUPAC name 1-[1-hydroxy-2naphthol azo]-2-naphthol-4-sulphonic acid sodium salt, its structure is given in Figure. 1. 10 ppm dye soultion was prepaed by taking 10 mg of Eriochrome Black T and dissolved in 1 lit of distilled water.

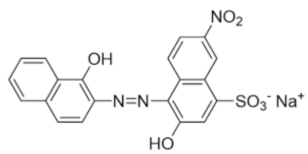

Figure 1. Structure of EBT azo dye

2.4 Adsorption studies

The experiment was carried by taking 30 ml of 10 ppm organic dye solution in a 100 ml beaker at room temperature. The solution was stirred with different dosage of nano powder and different reaction condition on a magnetic stirrer. The adsorption efficiency of γ-Fe_2O_3 was examined in the function of initial concentration of EBT dye, adsorbent dosage, pH and contact time. After stirring, the solution was centrifuged with fixed speed and time and the filtrate was taken into a dry test tube. The filtrate was analyzed for the residual using UV-Vis spectrometer. The percentage of adsorption EBT dye adsorbed from aqueous solution with the γ-Fe_2O_3 was calculated using Eq.

$$\%Adsorption = (C_0\text{-}Ce)/C_0 \times 100 \quad \text{------(2)}$$

Where C_0 and C_e are the initial and equilibrium concentration of dye respectively.

3. Results and Discussion

3.1. Powder X-Ray Diffraction studies

The PXRD pattern of the as-prepared γ-Fe_2O_3 nano powder is shown in the Figure 2. The PXRD spectrum shows that the nano powder is crystalline with hexagonal phase and matching well with data reported in literature [12]. Presence of diffraction peaks in XRD spectra of the samples at 2θ=24.1°, 33.1°, 36.0°, 40.8°, 49.4°, 54.0°, 57.4°, 62.4°, and 63.9° were in good agreement with the corresponding (012), (104), (110), (113),(024), (116), (214) and (300) diffraction planes of γ-Fe_2O_3 respectively and clearly indicate the formation of γ-Fe_2O_3 phase. Along with Fe_2O_3 a small peak of

Fe_3O_4 secondary phase was also detected. The average crystallite size was estimated from Scherrer's formula [13] and was found to be 30-40 nm respectively.

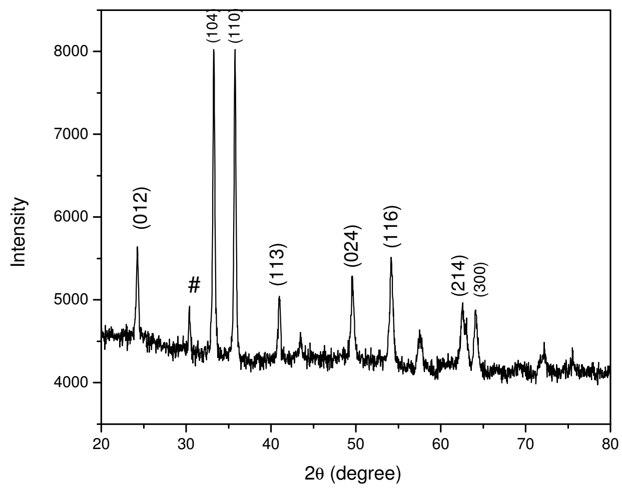

Figure 2. PXRD spectrum of γ-Fe_2O_3 nano powder (# Fe_3O_4 impurity peak).

3.2 Scanning Electron Microscopy

The SEM photograph of the as-prepared γ-Fe_2O_3 nano powder is shown in Figure 3, it can be seen that the nano particles are agglomerated and fluffy with porous morphology. The voids and pores present in the sample can be attributed to the liberation of large amount of gases produced during the combustion synthesis [5]. The average size of the agglomerated particles is 0.5 to 3 µm.

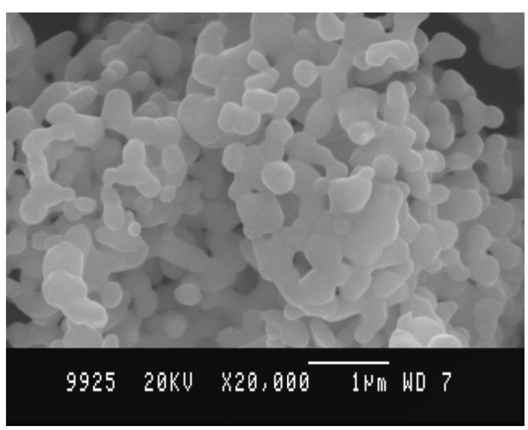

Figure 3. Scanning electron micrograph of γ-Fe_2O_3 nanopowder prepared by Solution combustion method

3.3 Fourier Transform Infrared Microscopy

The FTIR spectra were recorded using the KBr beam splitter in the mid IR region from 4000 to 400 cm^{-1}. The characteristic region between 2000 and 400 cm^{-1}. is shown Figure 4. There are two peaks appearing at 450 and 537 cm^{-1}, which can be ascribed to the Fe-O vibration of the γ-Fe_2O_3 nanopowder. The peak at about 3400 cm-1 corresponds to H-OH stretch.

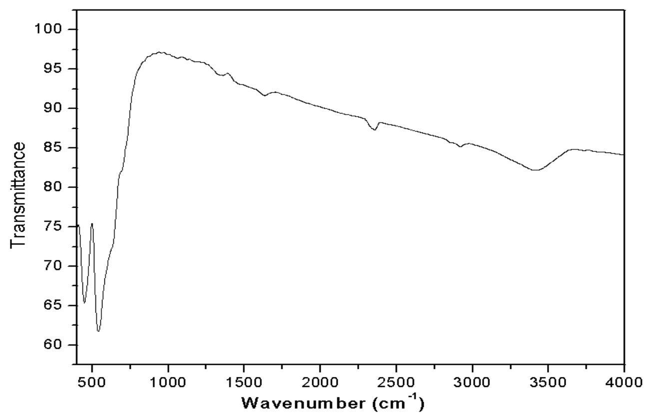

Figure 4. FTIR spectrum of γ-Fe_2O_3 nano powder.

3.4 Adsorbent studies

3.4.1 Effect of Adsorbent dosage

The loading efficiency of an adsorbent can be determined by varying the γ-Fe_2O_3 adsorbent dosage from 5 mg - 50 mg. As elucidated in Figure 5. The efficiency of EBT adsorption was increased from 19 % to 34 % when the adsorbent dose increases

from 5 mg to 40 mg. The efficiency of adsorption increases with increase adsorbent dose was due to increase in surface area and availability of more active sites. On further increasing of dosage above 40 mg the adsorption efficiency decreases due to overlapping of adsorption sites as a result of overcrowding of adsorbent [3]. The maximum decolorization observed at 40 mg where the initial concentration of 10 ppm and contact time of 10 minutes.

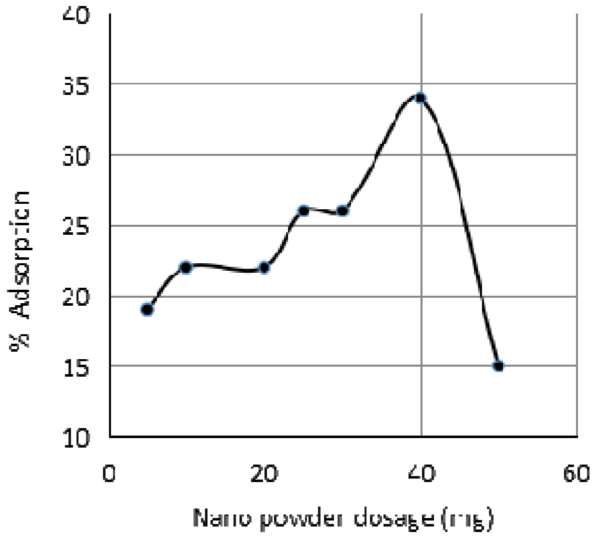

Figure 5: Effect of dosage on adsorption

3.4.2 Effect of contact time

To study the effect of contact time on the rate of adsorption, 30 ml of 10 ppm dye solution was taken in 100 ml beaker and optimized dosage of 40 mg of nano powder was added to it. The solution was stirred on a magnetic stirrer for the time intervals of 5, 6, 8, 10, 13, 15, 20, 25 minutes. UV-Vis spectrometer reading was recorded for every trial of the solution and results are shown in the Figure 6. From the figure it can be noticed that the maximum adsorption efficiency of 49 % was found at the contact time of 8 minutes. The adsorption characteristics indicated a rapid uptake of the dye from 5 -8 minutes. The adsorption rate decreases with further increase in contact time because of all available sites was covered, and no active sites available for binding [2].

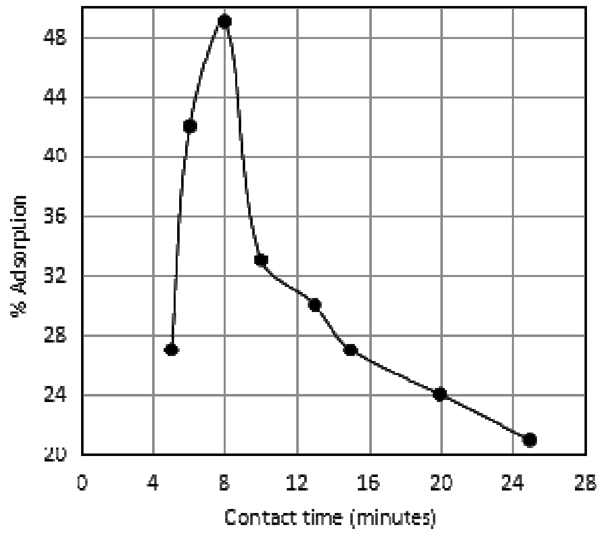

Figure 6. Effect of contact time

3.4.3 Initial dye concentration

The initial dye concentration shows the capacity of adsorbent in adsorption process. Figure 7 shows that, rapid adsorption in the beginning, further % adsorption of EBT was decreased, it is due to increase in dye concentration. As shown in graph when initial dye concentration was increased from 5 ppm to 20 ppm the adsorption efficiency of γ-Fe_2O_3 particles, decreased from 71% to 37% (5 ppm) respectively keeping adsorbent dosage constant. The reason for decrease in adsorption efficiency with initial dye concentration is may be due to the dye agglomeration and the reduction of mobility of the adsorbed aggregates. Hence, a lower initial dye concentration may enhance the adsorption process.

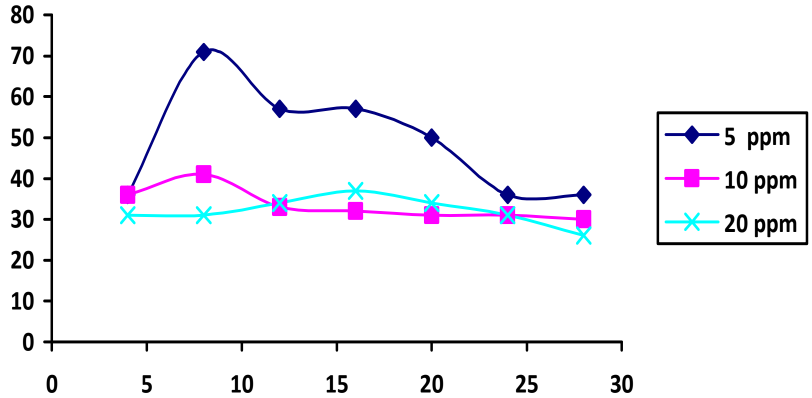

Figure 7. Effect of initial dye concentration.

4.0 Conclusion.

In this study, the adsorption of EBT from its aqueous solution was investigated. γ-Fe_2O_3 was prepared by low temperature solution combustion method, these nano particles with average size less then 3µm in diameter are used in the removal of the azo dyes. The optimum conditions of various parameters obtained were 10 ppm initial dye concentration, 40mg adsorbent dosage, and at room temperature and of 8 minutes of contact time. The above results reveal the usage of γ-Fe_2O_3 nanosized powder, to be effective adsorbent for the purification of contaminated water.

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