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Article

TREATMENT OF DYES CONTAINING WASTE WATER WITH NANOCRYSTALLINE ZINC FERRITE

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ABSTRACT

Treatment of colored water before discharged is an important issue in order to avoid certain hazards and environmental problems. In contrast with the conventional methods of dyes removal the adsorption techniques is the most versatile and widely used, in special when the adsorbent could easily be removed through magnetic separation. Therefore in order to accomplish these conditions in the present paper was obtained zinc ferrite to be used as adsorbent in the treatment process of waste waters containing dyes. The nanocrystalline zinc ferrite was obtained after a heating treatment of the zinc ferrioxalate coordination compound, as precursor, at 500^{o}C. The obtained zinc ferrite was investigated by IR spectroscopy, X-ray diffraction and SEM microscopy.

Keywords: zinc ferrite, dye, adsorption.

1. INTRODUCTION

The release of colored water in the effluents, besides the pollution with heavy metals, poses certain hazards and environmental problems. Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries.

These colored compounds are not only aesthetically displeasing but also persist for long distances in flowing water, retards photosynthesis, inhibit growth of aquatic bi ota by blocking out sunlight and utilizing dissolved oxygen [1-6].

There are various conventional methods of removing dyes including coagulation and flocculation, oxidation or ozonation and membrane separation [7-15]. However, these methods are not widely used due to their high cost and economic disadvantage. Chemical and

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electrochemical oxidations, coagulation are generally not feasible on large scale industries. In contrast, an adsorption technique is by far the most versatile and widely used. [1, 7, 9, 15-18] Several adsorbents have been investigated by the previous researchers such as: activated carbon, alumina, silica, natural materials and synthetic resin [15, 19-23]. The most adequate adsorbent has to accomplish the following requirements: to be a low cost adsorbent to be easy regenerated and disposed. Furthermore in the last years an important accent was out on the separation and regeneration of the adsorbent from heterogeneous systems. In this way a lot of separation technique such as free settling, centrifugation, and membrane filtration has been studied. Unfortunately, these separation techniques suffer from prolong usage of equipment operation, complicated technical requirements as well as high operational costs and thus severely restrict water treatment applications. Being an efficient and economical method, magnetic separation would be an ideal alternative than centrifugation or filtration methods [1]. Therefore the use of various types of magnetic nanoparticles has been reported for the removal of different pollutants from environmental samples [1, 9, 16, 17, 24-26]. In this paper the nanocrystalline zinc ferrite was used as adsorbent material for the treatment of waste waters resulted from the remanufacturing of the empty ink cartridges. The zinc ferrite was obtained by thermal decomposition of zinc ferrioxalate coordination compound, as precursor, this method had been widely used for synthesis of nanoferrites [27, 28].

2. MATERIALS AND METHODS

All the reagents used for the synthesis of ferrite were analytical grade, including ferric (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Mw = 403.95 $gmol^{-1}$, Merk), zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, Mw = 297.49 $gmol^{-1}$, Merk), 1,2-ethanediol ($C_2H_4(OH)_2$, Mw = 62.07 $gmol^{-1}$, Merk) and 2M nitric acid solution (Merk). An aqueous solution containing ethanediol, iron nitrate, zinc nitrate and nitric acid (2M) in a molar ratio x : 2 : 1 : y where $x \geq 3$ and $y \geq 2$ is heated in a water bath. The reaction is completed when no more gas evolving is observed. The obtained solid reaction product, purified by refluxing with an adequate acetone-water mixture, is filtered, washed with acetone and maintained in air until constant mass. The coordination compound $[Fe_2Zn(C_2O_4)_4(OH_2)_6]$ precursor is synthesized using 2M nitric acid solution. The oxide $ZnFe_2O_4$ is obtained after heating treatment of the precursor at 500^oC for one hour, with a heating rate of 5^oC/min.

The FTIR spectrum (KBr pellets) of the ferrite was recorded on a Vertex 70 BRUKER-FTIR spectrophotometer in the range 400-4000 cm^{-1}. The oxide was characterized by X-Ray diffraction (XRD) analysis. The powder X-Ray diffraction patterns of the obtained oxides was recorded at room temperature with a XRD using a Rigaku Ultima IV diffractometer, using Cu K_α radiation (λ = 1.5418 Å). SEM image was recorded using a Quanta FEG 250 microscope, equipped with an EDAX ZAF quantifier.

The obtained zinc ferrite was used as adsorbent material in the treatment of waste waters resulted from ink jet manufacturing. The residual solution containing dyes was obtained from a local manufactory were the empty ink-jet cartridges are refilled. The analyze of the dye concentration from the solution before and after adorption process was realized spectrophotometricaly using a Varian Cary 50 spectrophotometer. The spectra were recorded in the range of 300-800 nm. In the first step the influence of the adsorbent quantity upon the degree of adsorption was determined. In this way 25 mL of residual waters was treated with various quantities of adsorbent materials (0.02, 0.03, 0.04, 0.05, 0.06 and 0.07 g). The samples were shacked from 1 hour using a Julabo SW23 shaker, and after were filtrated and

the resulted solutions were again analyzed through UV-VIS spectrophotometry. After establishing the optimum S: L ratio the influence of the shaking time (15, 30, 45, 60, 90 and 120 min) upon the adsorption capacity was determined. The degree of adsorption was determined based on the following equation:

$$\eta = \frac{(Ads_{init} - Ads_{fin})}{Ads_{init}} 100 \quad (1)$$

where:

η represents the removal degree of dye, %;

Ads_{init} represents the initial absorbance of the dye present in the waste water;

Ads_{fin} represents the absorbance of the dye present in the waste water after treatment with the zinc ferrite.

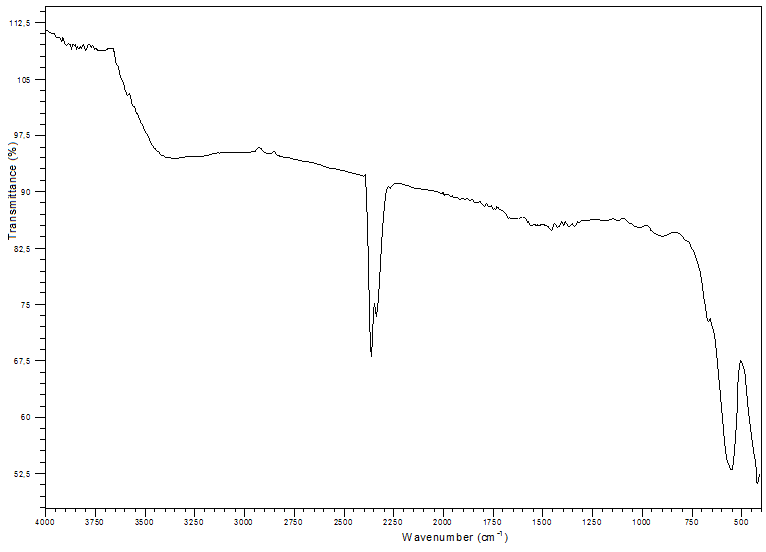
3. RESULTS AND DISCUSSIONS

The synthesis reaction of the zinc ferrioxalate is based on the redox reaction between 1,2-ethanediol and nitrate ion [27]:

$$12C_2H_4(OH)_2 + 6([Fe(OH_2)_6]^{3+} + 3NO_3^-) + 3([Zn(OH_2)_6]^{2+} + 2NO_3^-) + 8(H^+ + NO_3^-) \xrightarrow{\Delta t^\circ} \xrightarrow{\Delta t^\circ} 3Fe_2Zn(C_2O_4)_4 \cdot 6H_2O_{(s)} + 32NO_{(g)} + 76H_2O_{(g)}$$

The FTIR spectrum (Figure 1) of the conversion product obtained after the calcination at 500 °C for 1h of the coordination compound shows only the bands characteristic for $ZnFe_2O_4$ ferrite (550cm-1 and 418 cm-1) being in agreement with the literature data [29, 30].

Figure 1: FTIR spectrum of zinc ferrite

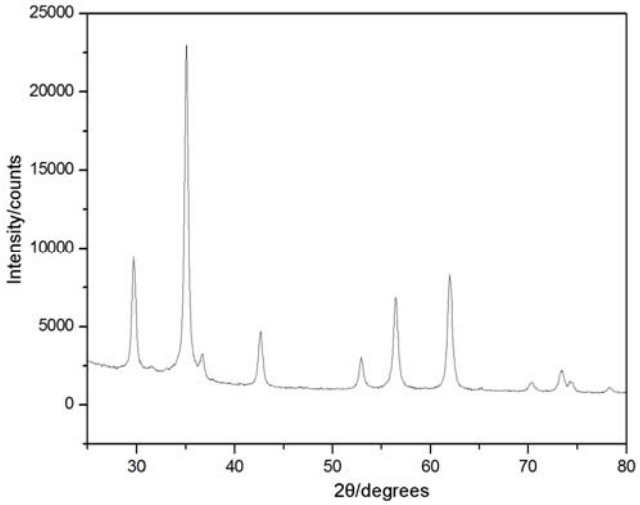


In Figure 2 is presented the XRD pattern of $ZnFe_2O_4$ ferrite. The XRD pattern shows the presence of well crystallized pure zinc ferrite was identified in using JCPDS 04-006-8036 (8.460Å). The average crystallites size was evaluated using Scherrer's formula [31]:

$$d_{XRD} = [0.91\lambda/(\beta\cos\theta)] \times 57.32 \quad (2)$$

where d_{XRD} is the crystallite size, λ the wave length (Cu K_α), β the corrected half-width obtained using α quartz as reference and the Waren formula and θ is the diffraction angle of the most intense diffraction peak.

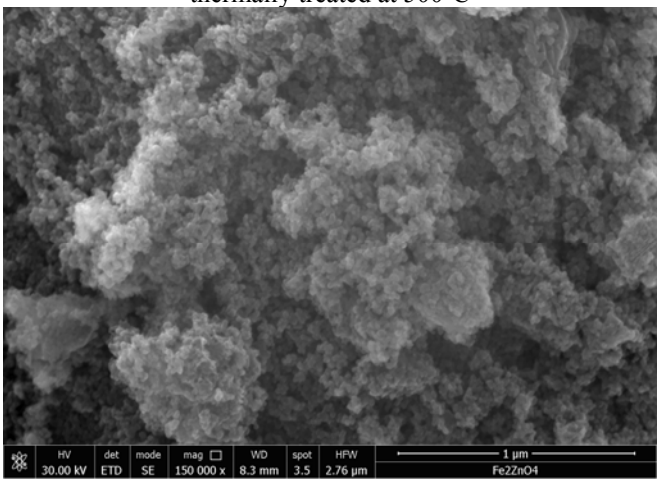
Figure 2: The XRD of $ZnFe_2O_4$ derived from $[Fe_2Zn(C_2O_4)_4(OH_2)_6]$ compound obtained by an independent pyrolysis at 500°C



The mean crystallite size evaluated using Scherrer's formula is 22 nm and the lattice parameter from XRD analysis is 8.453Å.

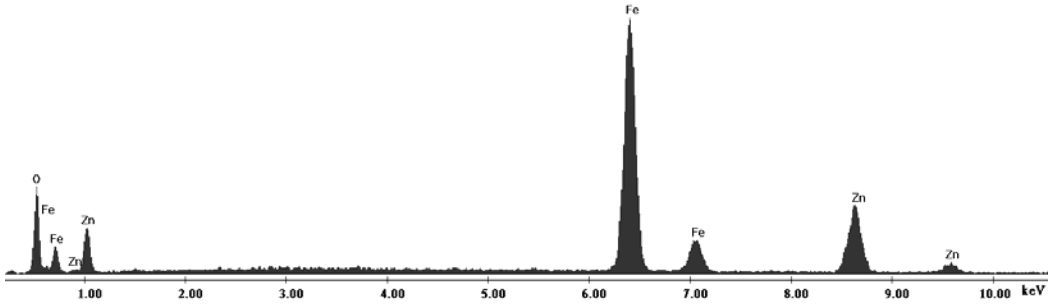
The SEM image (Figure. 3) shows that the ferrite consists of agglomerated spherical particles with 20-40nm average particle size and microporous structure.

Figure 3: SEM image of $ZnFe_2O_4$ powder prepared from $Fe_2Zn(C_2O_4)_4(OH_2)_6$ compound thermally treated at 500°C



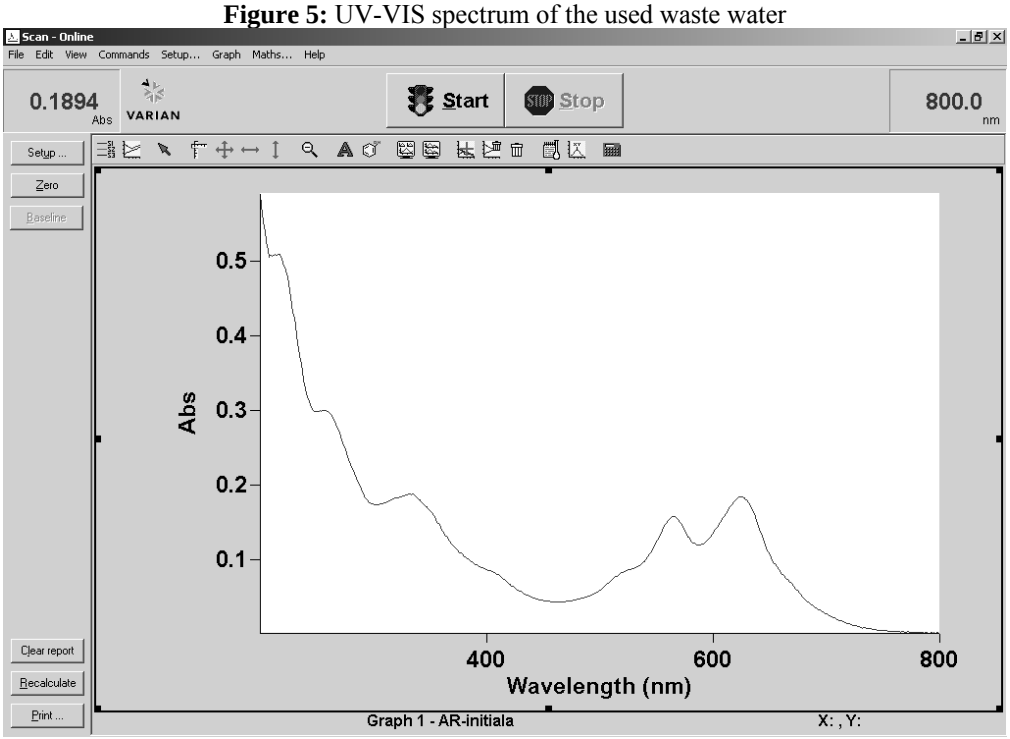
The EDX spectrum of $ZnFe_2O_4$ is presented in Figure 4. Qualitative and quantitative EDX analyzes showed a high purity and corresponding stoichiometry of the zinc ferrite analyzed.

Figure 4: EDX spectrum of $ZnFe_2O_4$ powder prepared from $Fe_2Zn(C_2O_4)_4(OH_2)_6$ compound thermally treated at 500°C



The UV-VIS spectrum of 300-800 nm of the waste waters treated with the studied adsorbent is presented in Figure 5.

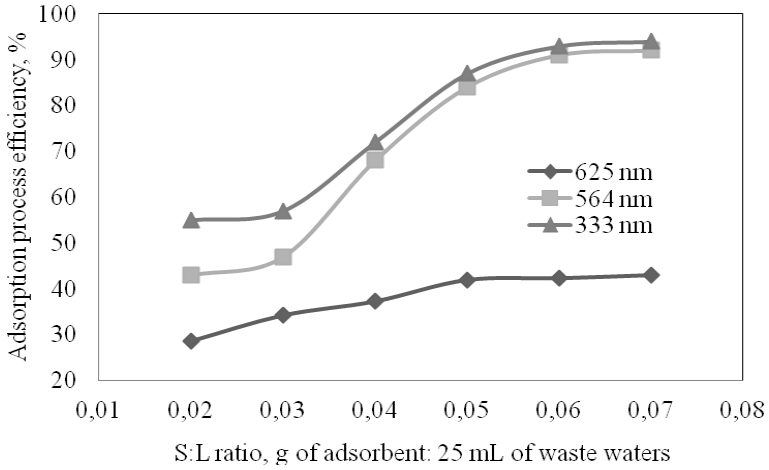
Figure 5: UV-VIS spectrum of the used waste water



In the spectrum presented in Figure 5 can be observed three peaks at three wavelength (625, 564 and 333 nm) specific for the three colors present in the waste waters.

The influence of the S:L ratio upon the efficiency of the adsorption process of the three colors present in the waste waters onto the studied zinc ferrite is presented in Figure 6.

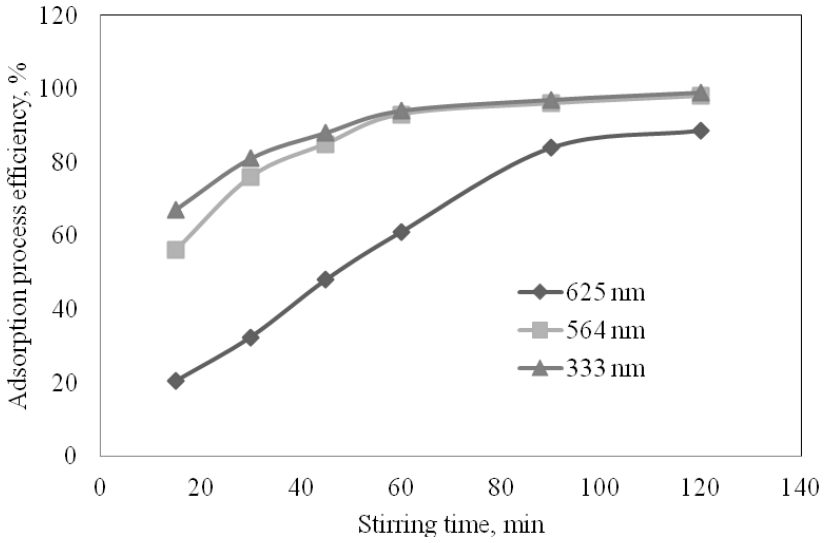
Figure 6: The influence of the S:L ration upon the adsorption process efficiency



From the experimental data can be observed that for the all colors present in the studied waste waters the use of a higher quantity of zinc ferrite lead to a higher degree of separation of dyes from aqueous solution. This influence is not significant for a S:L ratio higher than 0.05 g of zinc ferrite in 25 mL of waste waters. Therefore the further studies will be conducted at this S:L ratio

The influence of the stirring time upon the efficiency of the adsorption process of dyes onto the studied zinc ferrite is presented in Figure 7.

Figure 7: The influence of the stirring time upon the adsorption process efficiency



It can be observed that for the removal of dyes which absorb at 564 nm and 333 nm a stirring time of 60 minutes is sufficient for obtaining an adsorption degree higher than 90%. But to remove all the colors present in the waste waters and realize 100% treatment efficiency is necessary to treat the waste waters with the studied adsorbent for 120 minutes.

4. CONCLUSION

Nanocrystalline zinc ferrite, with pure spinelic phase $ZnFe_2O_4$, was obtained after the calcination zinc ferrioxalate coordination compound at 500˚C. The FT-IR spectrum showed two characteristic metal oxygen vibrational bands. The average particle size of ferrite was in the range of 20-40 nm, as revealed by XRD and SEM techniques.

The obtained nanocrystalline zinc ferrite presented good efficiency in the removal process of dyes from a real waste water. The highest degree of separation of the dyes from the waste water resulted from the ink-jet cartridges remanufacturing is obtained when is used a S:L ratio of 0.05 adsorbent in 25 mL of waters for 2 hour of shaking.

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