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Evaluation of the response to chromium removal of zinc ferrite synthesized by different methods

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Abstract. In this project, it was synthesized zinc ferrite by different methods to compare the synthesis effect in chromium adsorption. The material was characterized by using infrared (IR) spectroscopy and Raman spectroscopy found a spinel-type zinc ferrite, their response for chromium removal was analyzed using UV-Vis spectroscopy.

Keywords: solvothermal, solid-state, polyester-combustion, combustion, microwave.

1 Introduction

Chromium compounds are widely used in many areas of industry such as chrome plating, electronic, metallurgical, wood processing, leather tanning, textile dyeing, steel manufacturing, pigments synthesis, minery and even in nuclear power plants [1-8]. This element exist in many oxidation states, the most common are hexavalent and trivalent, Cr(VI) and Cr(III) respectively, being Cr(VI) more toxic than trivalent one, due to the health risks for living organisms, as a carcinogenic and mutagenic component. Because of this, the United States Environmental Protection Agency (USEPA), the Agency for Toxic Substances and Disease Registry (ATSDR) and the World Health Organization (WHO) limit the Cr(VI) concentration between 50 ppb and 100 ppb for drinking water [1-3].

Actually, exists several methods to removal chromium from wastewaters, the most commonly used is adsorption which is consider to be simple and economical. In recent works, different materials had been used, such as TiO2 either alone or functionalized [1, 3], carbon compounds [8, 9], metallic nanoparticles [5] and spinel-type ferrites with magnetic properties [2, 4, 7, 8] for removal chromium via adsorption method. Furthermore, it has been proven that the best removal is under acidic conditions (pH under 3) [2, 4-6, 8, 9] for all the materials that have been used.

Hang et al. [7] studied the response of zinc ferrite and a composite of zinc ferrite with iron oxide for chromium removal and observed promising results. Hu et al. [2]

made a comparison between different spinel-type ferrites and found that the best for chromium removal was manganese ferrite under a pH of 2.

In this work it was synthesized zinc ferrite by five different methods who gave it different properties, this to evaluate the change in its response to chromium removal by adsorption under sunlight for an appropriate time exposure.

2 Experimental Procedure

The zinc ferrite was prepared by five different methods explain below. For solid state 2.4 g of Fe2(SO)4 and 0.5 g of ZnO were weighted, both compounds were milled in an agate mortar and it was added 3 ml of acetone and still milled, after that the powder was put in a melting pot inside a oven (Mulfa Terlab, México) for 2 hrs at 400°C with a heating rate of 10°C/min. After 2 hours at 400°C, the melting pot was let to cool down and the powder milled again. Next the sample was heated up to 800°C for 2 hours without heating rate, after the 2 hours it was let to cool down, milled and put into the oven at 1000°C for 12 hours.

The reaction under solvothermal method was carried out with 4.07g of Fe(NO3)3-9H2O, 1.50 g of Zn(NO3)2-6H2O and 0.05 g of polyethylene glycol (PEG). The nitrates were dissolved in 50 ml of tridistilled water and the PEG was dissolved in 40 ml also of tridestilled water. Afterwards the nitrates and the PEG were mixed and shaken by ultrasonic bath, after that it were added NaOH to achieve a pH near to 11. Next the solution was poured into a teflon container and this container was put in the stainless-steel reactor, the reactor was put into an oven for 24 hours at 175°C. The solution inside the reactor was filtered in vacuum and rising with tridistilled water until get a pH near 8. The powder on the paper was placed in a oven at 80°C for 4 hours.

For polyester-combustion method, the same precursors and the same proportion as in solvothermal were used. Meanwhile, in a crystallizer were put 20 ml of distilled water and 20 ml of ethanol and after it started to heating up. When the solution was around 50°C it was added citric acid and next the nitrates, it continued heating up and around 70°C it was added 3 ml of PEG. It continued heating up and before it reached 90°C, 5 ml of ammonium hydroxide were added. After that, the crystallizer was let to cool down at room temperature in order to form a gel and next it was put into an oven at 400°C, once the combustion occurred it was milled and then it was calcined at 700°C for 14 hours.

The combustion method is too similar with polyester combustion one, it were weighted 4.08 g of Fe(NO3)3-H2O, 1.02 g of Zn(NO3)2-H2O, 2.42 g of urea and 0.83 g of boric acid. All the precursors were dissolved in 20 ml of tridestilled water, the solution in a beaker was put into an oven and heating up at 620°C to make the combustion. After that, the sample was milled for 5 minutes and the powder was collected.

The solution that was used in solvothermal method also it was used for microwave, that solution was put into a container and placed in a microwave machine (1200 W). The procedure consisted on heating up 30 seconds, after that, let to cool down and again heating up for 60 seconds, this was repeated increasing the heating time by 30 seconds until get a heating time of 120 seconds.

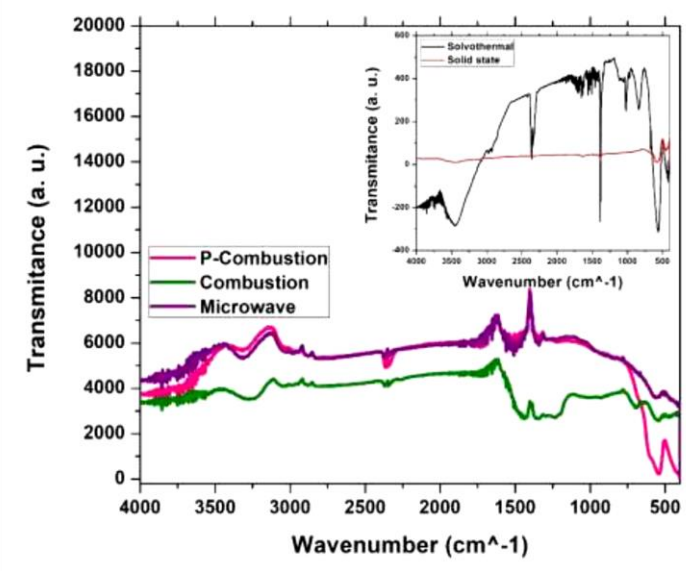

Fig. 1. IR spectra from zinc ferrite synthesized by five different methods such as solid state, solvothermal, polyester combustion, combustion and microwave.

The solution was filtered in vacuum with distilled water until getting a pH near 8. The sample in the paper was placed into an oven at 110°C for 4 hours and then the powder was collected.

For Raman spectroscopy a Witec Alfa 300-A was used with a laser beam of 630 nm and a 20x objective. The IR spectroscopy was realized in a Thermo Scientific Nicolet iS5. For the UV- Vis characterization, 20 mg/L potassium dichromate solution was prepared measuring its absorbance in a CARY 5000 UV-Vis-NIR spectrophotometer, after that 100 mL of the solution was added to approximately 0.05 g of zinc ferrite of each different route of synthesis. Afterwards the bottles were exposed to sunlight under constant agitation. Finally, the solutions were filtered by a cellulose filter (0.44 μm) and UV-Vis measured at different times (15 minutes, 1 hour, 2 hours, 3 hours and 4 hours).

3 Results

Figure 1 shows the IR spectra from each zinc ferrite synthesized by different methods, it could be observed that the vibrational and rotational modes in the octahedral groups depend on the position of the cation in their structure. The characteristic bands of spinel-type structure shown two regions over the infrared spectra. The bands between 800-600 cm^{-1} result for the tetrahedral position of zinc, the high frequency bands ν_1(549-555 cm^{-1}) and ν_2 (422-383cm^{-1}) are attributed to the vibration of Fe^{3+} ions in both tetrahedral and octahedral positions, respectively [10]. The vibration bands over 600-400 cm-1 were in our case, zinc ferrite spinel type were highly observed at around

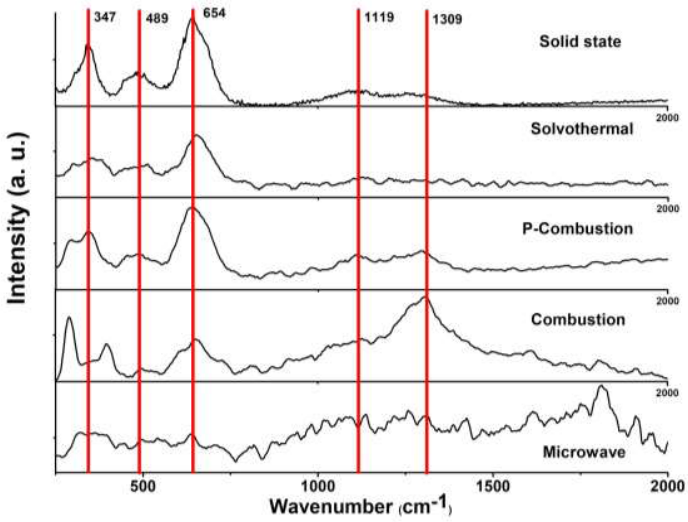

Fig. 2. Raman spectra from zinc ferrite synthesized by five different methods such as solid state, solvothermal, polyester combustion, combustion and microwave.

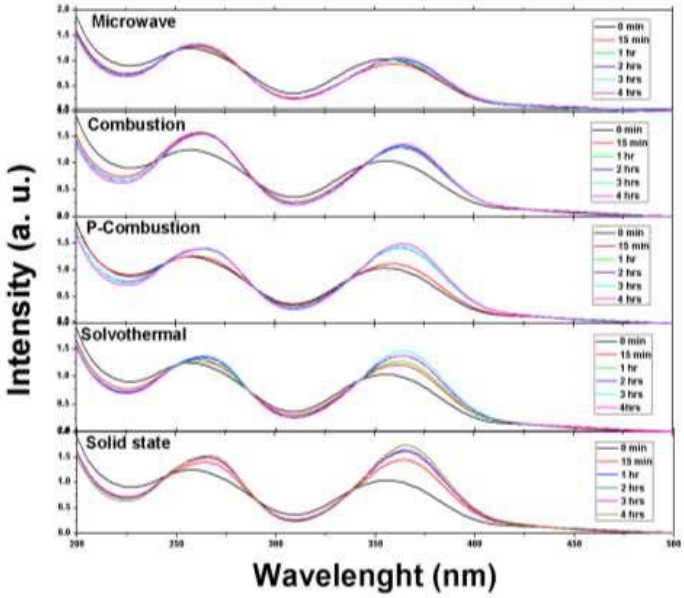

Fig. 3. Absorbance spectra of potassium dichromate treated with zinc ferrite synthesized by five different methods such as solid state, solvothermal, polyester combustion, combustion and microwave.

541 cm^{-1} determined the elongation of Fe-O which correspond to octahedral coordination [11, 12].

In Figure 2, it can be observed the Raman spectra of $ZnFe_2O_4$ synthesized by the five ways presented above, and according the previous published data [13]. As it was reported, the space group of the cubic spinel zinc ferrite is O^7_h (F*d3m*) with eight formula units per unit cell.

There are five first-order Raman active modes according to the group theory ($A_{1g} + E_g + 3F_{2g}$) [14], and theses modes were observed in the range of 200–800 cm^{-1} ($F_{2g(1)}$ in 221, E_g in 246, $F_{2g(2)}$ in 355, $F_{2g(3)}$ in 451 and A_{1g} in 647)[10]. In figure 2, the Raman spectra show a band at above 600 cm-1 that corresponds to the motion of oxygen in tetrahedral AO_4 group besides presents other low frequency bands (347 cm^{-1} and 489 cm^{-1}) which correspond to the octahedral BO_6 site [15]. The bands obtained at ~1119 cm-1 and ~1309 cm−1 could not be assigned to a particular mode.

In Figure 3, there are displayed the potassium dichromate solutions at a pH around 6 was used in order to compare the different routes of synthesis of zinc ferrite and observed the effect in chromium VI removal. The present species, according to this pH, gave an intense yellow color to the solution. The pH is a parameter, which it could appreciate in oxide-reduction equilibrium from chromium because the medium affects the ionization level and the main zones for species while the reaction is made.

The surface of the zinc ferrite has a positive charge with this pH and the species of chromium has a negative charge, so it was expected the adsorption of chromium. By the way, the forces of attraction and repulsion between the medium and the ferrite is going to be affected by the pH due to it will be affected the equilibrium of the reaction.

Observing this figure 3, it shown a displacement of the band due to the generation of ionic species, with a constant increase after three hours. This is because the reaction reach a maximum adsorption between the chromium species and the surface of the ferrite.

4 Conclusions

The IR and Raman spectra suggest that spinel-type zinc ferrite was synthesized by different methods, and presented in major proportion at solid state, solvothermal and polyester combustion. The solution rapidly reached the maximum chromium adsorption affected by the PH solution, it suggests a change in PH solution could represent a better adsorption, and according to the previous data at low pH the oxide-reduction equilibrium is promoted and derives to a better chromium adsorption.

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