



GREEN SYNTHESIZED Fe₃O₄ NANOPARTICLES FOR LANASYN RED AZO DYE REMOVAL FROM AQUEOUS SOLUTIONS

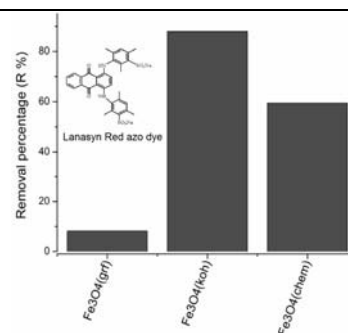
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In this study, the removal efficiency of Fe₃O₄ (grf) and Fe₃O₄ (koh) nanoparticles was compared with the removal efficiency of Fe₃O₄ (chem). The characterization of all synthesized magnetic adsorbents was carried out using conventional techniques such as FT-IR, TEM, XPS and VSM. The dye removal was tested for all nanoparticle samples. The effect of various experimental parameters such as initial dye concentration, pH, contact time and adsorbent dose on the removal of Lanasyne Red was investigated. A higher removal percentage was achieved with Fe₃O₄ (koh) NPs (82.4%) in comparison with Fe₃O₄ (grf) NPs (14.9%). The prepared Fe₃O₄ (koh) NPs could thus be used as promising adsorbent for removal of Lanasyne Red from polluted water.



INTRODUCTION

The dyes presence in wastewater, even after treatment, can have side effect on the environment. These azo dyes are most commonly used in textile industry and are very stable in the environment (half-lives of 2–13 years), causing toxicological problems to the aquatic environment and major health problems to humans.^{1,2}

With the growing concerns on health, the removal of dyes became of prime importance, having a great influence on the environment quality by their presence in water. The conventional dye removal techniques (coagulation, flocculation, adsorption, and membrane filtration) are using different toxic chemicals leading to an incomplete degradation process. Among treatment technologies, adsorption rapidly gaining prominence as a method of treating aqueous effluent because

has advantages such as: the possible adsorbent regeneration at low cost, simplicity of design and ease of operation.^{3,4}

Recent studies present the potential of nanomaterials such as metal and metal oxide nanoparticles for water remediation in order to remove the pollutants. The traditional methods which are used for extensive production of metal and metal oxide nanoparticles require the use of very reactive and toxic reducing agents.^{5,6} These toxic substances can cause negative impacts on the environment. Therefore, the researchers continue to develop efficient and reliable green chemistry processes.⁵ In this regards, currently used clean, feasible and eco-friendly raw materials to produce nanoparticles which are functionalized and present good stability⁵ as biopolymers,⁷ ascorbic acid,⁸ amino acids,⁹ sugar and glucose¹⁰ are ones of capping biocompatible materials. Other biomaterials

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like leaf,¹¹ fruit,¹² seed¹³ and plant peel extract¹⁴ were used as eco-friendly raw materials in order to produce nanoparticles. The green synthesis presents a major interest due to its advantages represented by cost effective, environment friendly features, easy scaling up and no need of high it can be easy scaled up for using it at large scale synthesis and there is not needed the use of high energy, pressure, temperature and chemicals with toxic effects on environment⁵. From our knowledge, the use of grapefruit (grf) and kohlrabi (koh) extracts for the green synthesis of magnetite nanoparticles has not been reported. Also, the studies concerning the removal of Lanasyne Red azo textile dye are new.

The aim of this study was to remove the Lanasyne Red from aqueous solution using magnetite nanoparticles (Fe₃O₄ NPs) synthesized using grapefruit peel extract and kohlrabi leaves extract, a green and eco-friendly synthetic path. The synthesized nanoparticles were characterized by Fourier transform-infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and vibrating sample magnetometry (VSM). In order to find the optimal method for removal of the Lanasyne Red azo dye from the aqueous solution the effect of initial dye concentration, pH, contact time and adsorbent dose on removal was studied. The obtained results were compared with those with magnetite chemically obtained.

EXPERIMENTAL

Preparation of Fe₃O₄ nanoparticles with plant extracts

The Fe₃O₄ NPs were prepared by a method similar to previously used by Awwad and Salem.¹⁵ For this, the first time were obtained the aqueous extracts using 20 grams of raw vegetable material (peel or leaves) and 100 mL ultrapure water. The grapefruit peel and kohlrabi leaves used in the extraction were first washed to remove the adhering dirt and then wiped and shredded. Extraction was held at 70-80°C through magnetic stirring over 20 minutes at 900 rpm. The extract was filtered, and the volume was adjusted to 100 mL in a volumetric flask.

The NPs were prepared from FeCl₂·4H₂O and FeCl₃·6H₂O (molar ratio 1:2) dissolved in 100 mL distilled water, and the obtained mixture was heated to 80°C under moderate magnetic stirring. After 10 minutes were added 5 mL of plant extract, observing the color change of the reaction mixture from yellowish to reddish brown. Finally, after 5 minutes there were added 20 mL of 1 M NaOH solution dropwise in order to ensure a constant rate for precipitation uniformity and obtaining the Fe₃O₄ NPs. The synthesis takes place until the formation of a black precipitate. The mixture was cooled to room temperature, and the Fe₃O₄ NPs were separated with an

external magnet, washed with water and absolute ethanol, and dried in an oven at 50°C for 24h.

Characterization of nanoparticles

For morphological studies a drop of suspension of each sample was deposited and dried on a copper grid coated by a thin carbon layer prior to the electron microscopy analysis. The analysis was carried out using a Hitachi HD-2700 scanning transmission electron microscope (STEM), equipped with a cold field emission gun, working at an acceleration voltage of 200 kV and designed for HRTEM imaging with a resolution of 0.144 nm. Images were recorded and analyzed with the Digital Micrograph software from Gatan.

FT-IR spectra of samples were registered in the range 4000-400 cm⁻¹ with a JASCO 6100 FT-IR spectrophotometer by using the KBr pellet technique.

The XPS associated with Ar ion etching was used for qualitative and quantitative compositional analysis of nanocomposites, using a SPECS custom-built system. The excitation was made by using a dual anode Al (1486.6 eV) / Mg (1254.6 eV). In order to avoid artificial reduction of various oxidation states of the elements, etching was carried out with Ar ions accelerated to a maximum voltage of 1000 V and a filament current of 10 mA. Room-temperature magnetic behavior was recorded using a VSM produced by "Cryogenic Ltd."

The magnetic properties of the synthesized nanoparticles were measured with a VSM produced by Cryogenic. Magnetization curves were recorded at room temperature.

Adsorption measurements

The working solutions were prepared from a stock solution 1000 mg/L by diluting with deionized water to give the appropriate concentration of the working solutions. Adsorption of Lanasyne Red on Fe₃O₄ NPs was done under different conditions, such as: initial dye concentration (25–150 mg/L), contact time (10–60 min), pH (3–8) and adsorbent dosage (0.5–10 g/L). The initial pH of solutions was adjusted with 0.5 mol/L HCl and 0.5 mol/L NaOH solutions. The prepared Fe₃O₄ NPs were added to each flask contained Lanasyne Red and were continuously stirred at a constant speed of 400 rpm, at room temperature. The Fe₃O₄ NPs were separated with an external magnet and the supernatant was determined spectrophotometrically, by recording samples absorbance at 496 nm. Elimination yields of Lanasyne Red, R (%), were calculated as follows:

$$R, (\%) = (C_0 - C_t) / C_0 \times 100$$

where: C₀ (mg/L) represents the initial concentration of the solution, and C_t (mg/L) is the concentration of the solution at time t.

RESULTS AND DISCUSSION

Two samples of Fe₃O₄ NPs were obtained using vegetal extracts, samples abbreviated as follows: Fe₃O₄ (grf) - Fe₃O₄ synthesized using grapefruit peel extract, Fe₃O₄ (koh) - Fe₃O₄ synthesized using kohlrabi leaves extract, while Fe₃O₄ NPs synthesized by co-precipitation were denoted as Fe₃O₄ (chem).¹⁶

Nanoparticles characterization

TEM images and size distribution histogram for the two different samples (Fe₃O₄ (grf) and Fe₃O₄ (koh)) are presented in Fig. 1. As shown in this figure, both samples are roughly spherical particles and approximately monodispersed. The average particle size of Fe₃O₄ (grf) was found to be 14 nm with a minimum of 5 nm and a maximum size of

33 nm. In case of the Fe₃O₄ (koh) nanoparticles, the size varies between 3 and 25 nm with a mean value of 10 nm. The Gaussian fit (solid line) on histograms is showing a normal size distribution for both samples (Fig. 1). On the other hand, it is a good correlation between the size of Fe₃O₄ (grf) and Fe₃O₄ (koh) nanoparticles and specific surface area (when the nanoparticles size increases, the surface area decreases).

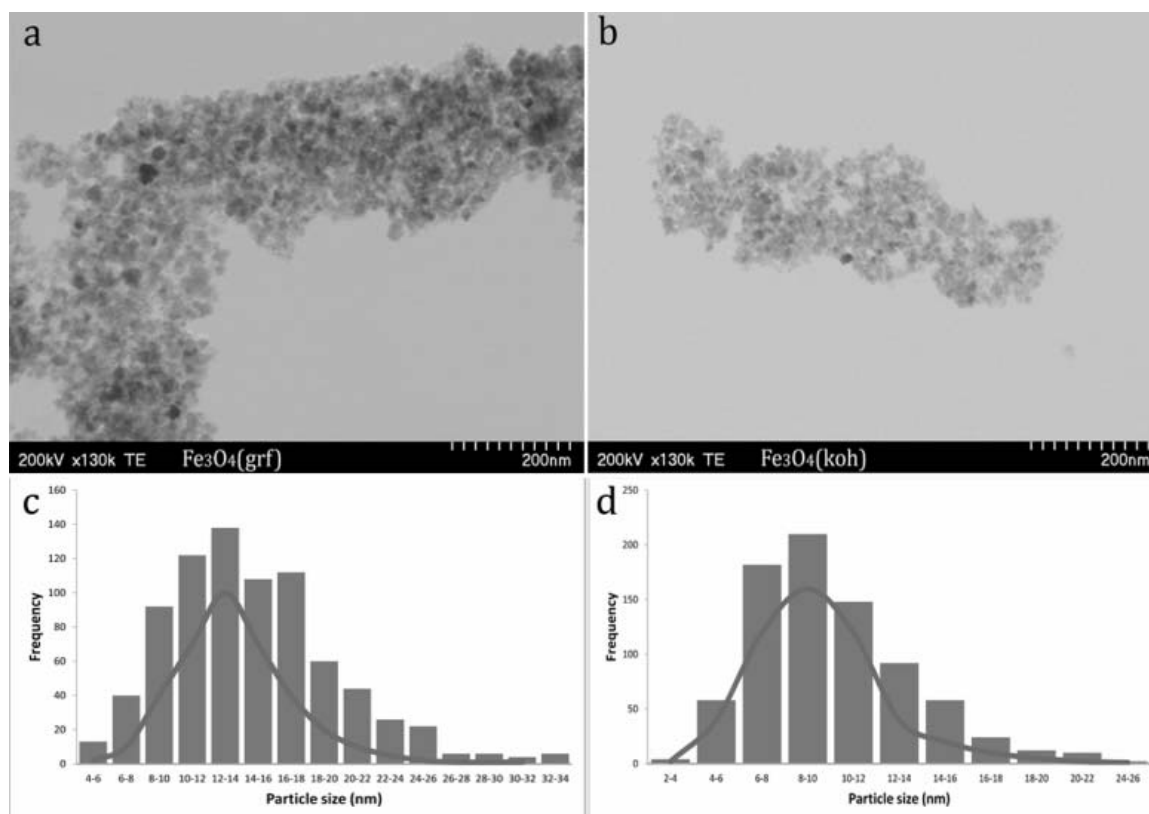


Fig. 1 – TEM images and histograms with Gaussian fitting for: (a-c) Fe₃O₄ (grf) nanoparticles, (b-d) Fe₃O₄ (koh).

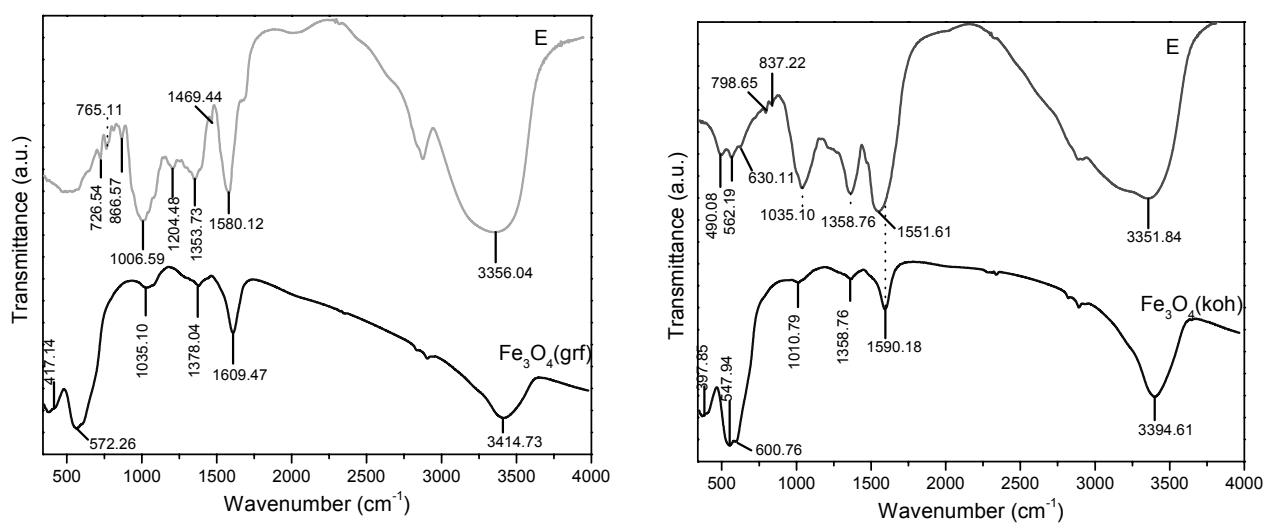
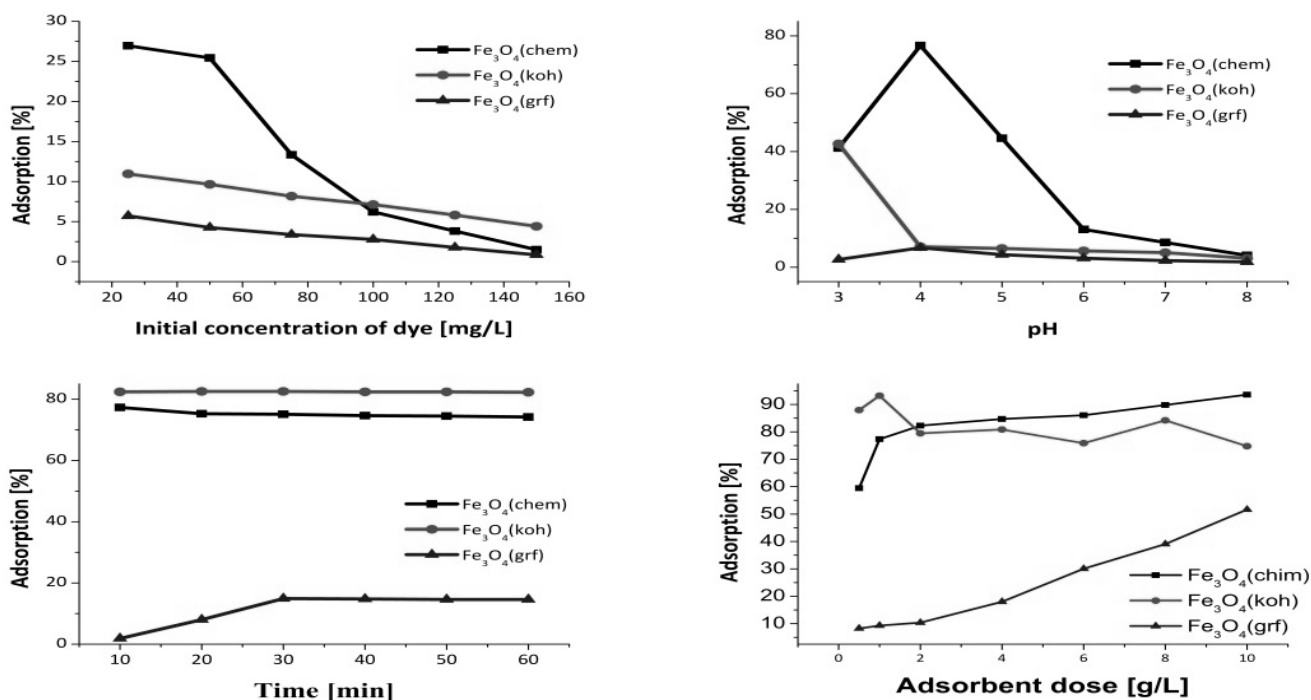


Fig. 2 – FT-IR spectra for extract powder (E) and Fe₃O₄ NPs from the green synthesis.

Table 1

XPS Fe 2p lines positions (eV); sat. - satellites.

Sample	Fe ²⁺ (3/2)	Fe ²⁺ (1/2)	Fe ³⁺ (3/2)	Fe ³⁺ (1/2)	sat.1	sat.2	sat.3	sat.4
Fe ₃ O ₄ (koh)	709.81	723.07	711.58	724.84	715.06	719.07	729.00	733.55
Fe ₃ O ₄ (grf)	709.28	722.54	711.22	724.48	714.65	718.43	729.00	733.44

Fig. 3 – Effect of investigated parameters on Lanasyne Red adsorption on the synthesized Fe₃O₄ NPs.

Infrared spectroscopy was used to further characterization of the dried form of synthesized Fe₃O₄ NPs as well of the dried form of kohlrabi leaves extract and grapefruit peel extract. The FTIR measurement was carried out to identify the bioactive components from vegetal extracts. The FTIR spectra of these NPs and vegetal extracts powder are presented in Fig. 2.

As it is shown in Fig. 2, the formation of Fe₃O₄ NPs can be observed by two strong absorption bands at around 572 and 417 cm⁻¹, 547 and 397 cm⁻¹ respectively, which, correspond to the Fe-O stretching band of magnetite (Fe₃O₄).¹⁵ The peaks at 3414 cm⁻¹ and 3394 cm⁻¹ were assigned to the phenolic OH groups, showing the involvement of the OH group in the stabilization process of formed nanoparticles.¹⁷ The absorption peaks at 1609 and 1590 cm⁻¹ were attributed to the N-H bending of amide group.¹⁸ The absorption peaks at 1378.04 cm⁻¹ and 1035.10 cm⁻¹, respectively 1358 and 1010 cm⁻¹ to the asymmetric and symmetric stretching vibration of COO.¹⁹

For XPS analysis, the following spectral lines were registered: Fe 2p, O 1s, N 1s and C 1s. The

C 1s positioned at 284.6 eV was used to calibrate the spectrum. XPS spectra deconvolution was performed with restrictions that took into account the relationships between the integrated intensity of the doublet spectral lines $p I(1/2) = (1/2) I(3/2)$. The separation of Fe 2p doublets (13.26 eV) was also accounted. For quantitative analysis the integrated intensities were calibrated using real sensitivity factors, transmission and medium free path of the computer program CASA. Fe 2p spectrum for investigated samples contains the lines attributed to Fe²⁺ and Fe³⁺ oxidation states. Two pairs of satellites also appear in the spectrum. The position lines are presented in Table 1.

As expected, the magnetization shows only a very small hysteresis loop, which is consistent with superparamagnetic behavior. The saturation magnetization and coercitive field values are 67 emu/g, 25 Oe for Fe₃O₄ (koh) sample and 62 emu/g, 18 Oe for Fe₃O₄ (grf) sample. The exchange field remains at low levels, <1 Oe. The results obtained for Fe₃O₄ (koh) and Fe₃O₄ (grf) were in accordance with those for Fe₃O₄ (chem).¹⁶

Adsorption behavior

Effect of dye concentration

Six different concentrations of Lanasy Red were selected to investigate the effect of initial concentration of dye on the synthesized Fe₃O₄ NPs. The amount of dye adsorbed after 20 minutes at initial pH of the solutions is graphed in Fig. 3. With the initial increase of Lanasy Red concentration from 25 to 150 mg/L, the adsorbed dye on the Fe₃O₄ NPs decreases. The adsorption of Lanasy Red from aqueous solution is dependent on its initial concentration. For subsequent analysis, the 25 mg/L concentration of Lanasy Red was used.

Effect of pH

The adsorption of Lanasy Red on Fe₃O₄ NPs varies with pH, because the value of pH affects both aqueous chemistry and surface binding sites of the adsorbents. The effect of pH on the adsorption of Lanasy Red was studied at room temperature at initial dye concentration of 25 mg/L, adsorbent dose of 0.005 g and contact time of 20 min. It was observed that the pH affects the adsorption of dye on the adsorbent and the maximum uptake of the Lanasy Red was obtained at pH of 3.0 for Fe₃O₄ NPs obtained with kohlrabi leaves extract and 4.0 for Fe₃O₄ NPs obtained with grapefruit peel extract and those obtained chemically.

Effect of contact time

The effect of contact time on adsorption capacity of Fe₃O₄ NPs for Lanasy Red was studied at initial dye concentration of 25 mg/L at pH 3.0 ± 0.4 and contact time of 20 min, at room temperature. The results indicate that the adsorbed amount of Lanasy Red increases with the increase of contact time, reaching equilibrium in about 10 minutes for the Fe₃O₄ (koh) NPs and Fe₃O₄ (chem) NPs and about 30 minutes for the Fe₃O₄ (grp) NPs.

Effect of Fe₃O₄ dose

The amount of adsorbent is one of the most critical parameters for rapid and efficient dye removal that must be optimized. It was observed that the percentage removal of Lanasy Red with rising adsorbent dosage increased with adsorbent quantity. A significant decrease in the removal percentage increase with the amount of Fe₃O₄ NPs

is due to the increase in specific surface area and reactive centers.

CONCLUSIONS

This work was focused on adsorptive removal of Lanasy Red on Fe₃O₄ NPs obtained using grapefruit peel extract and kohlrabi leaves extract. The extracts were used as eco-friendly precursors for preparation of magnetite nanoparticles. The amount of dye adsorbed was found to be dependent on the pH of solution, initial dye concentration, contact time and adsorbent dose. It was found that the removal efficiencies of Lanasy Red by adsorption onto Fe₃O₄ (koh) NPs, Fe₃O₄ (grp) NPs and Fe₃O₄ (chem) NPs were 82.4%, 14.9%, and 77.3%, respectively. Thus the Fe₃O₄ NPs obtained with kohlrabi leaves extract could be employed as alternative adsorbent to chemically obtained Fe₃O₄ NPs for Lanasy Red removal from aqueous solution.

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