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Synthesis and Characterization of Magnetic Nanoparticles with Plant Water Extract and their Application for Water Treatment

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ABSTRACT

Different amounts of Pomegranate (Punica granatum) peel water extract were added as antioxidant and stabilizer for iron oxide (magnetite) nanoparticles during their synthesis by co-precipitation method. The resultant particles were characterized by Fourier Transform Infra-Red (FTIR) spectroscopy to determine their structure. The magnetic properties of these particles were determined by vibrating sample magnetometers (VSM). Their particles size and crystallinity were measured by Transmission Electron Microscope (TEM) and X-ray Diffraction (XRD), respectively. FTIR results confirm that the formed iron oxide particles are reacted through the oxygen bond of CO group of the pomegranate peel water extract. The results of other measurements show that the produced particles had super paramagnetic properties and their sizes were in the range 3-19 nm. A sample of the prepared particles was tested for removal of methylene blue and red violet dyes from water at two different pH values.

Keywords: Magnetic nanoparticles, Plant water extract, Iron oxide, FTIR spectroscopy, Water treatment

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INTRODUCTION

Some industries such as textiles, leather, paper, cosmetics and food use dyes or pigments to stain their products. These industries especially textiles are the main sources for environmental pollution. Since most synthetic dyes are inert and are not easily biodegradable because of their molecular structures, so they became harmful to aquatic life when they wastes are discharged in water sources.

The stability of most dyes to oxidizing agents [1], photo- and bio-degradation led to the use of physical or chemical methods to remove dyes and pigments from the polluted water. The most widely used methods are adsorption techniques [2-6], in addition to electro-chemical [7,8], ultra-filtration [9] and coagulants [10]. Magnetite nanoparticles are attractiveparticles which have been generally utilized for many biomedical applications such as contrast material for magnetic resonance imaging [11-15], tissue particular arrival of restorative operators [16,17] hyperthermia [18,19] and attractive field helped radionuclide treatment [19]. Iron oxide nanoparticles are the essential decision as a result of their biocompatibility and synthetic soundness. Numerous blend techniques have been investigated for iron oxide nanoparticles. These incorporate natural dissolvable warming technique, polyol strategy, and co-precipitation technique [20-22]. The co-precipitation strategy is the best system for get ready watery scatterings of iron oxide nanoparticles on the grounds that the amalgamation is directed in water.

In recent years, magnetic nanoparticles have been received a high attention for their use to solve environmental pollution problems. Many authors have used Fe_3O_4 particles to adsorb heavy metals such as cadmium, nickel [23], arsenide and arsenate [24]. Then, the magnetic particles can be removed from the medium with the aid of magnet. Recently pomegranate pulp is used as a new biosorbents for removal of methylene blue from aqueous solution [25].

In the current work magnetite nanoparticles are synthesized by co precipitation method and different concentration of Pomegranate (*Punica granatum*) peel water extract are add as stabilizer and antioxidant. Only one prepared sample is tested for removal of methylene blue and red violet stain from assimilating polluted water.

MATERIALS AND METHODS

Synthesis of magnetic nanoparticles with plant water extract

All the used chemicals are analytical grade. Iron chloride hexahydrate (Riedel-deHaen), ferrous chloride heptahydrate (Fluka), ammonium hydroxide 28% (Edwek), Methylene blue (MB), Red violet dye (dystar) (RV) and 30% hydrogen peroxide were used in this experiment. Deionized water was deoxygenated by passing argon gas for 2 h before start. Fresh pomegranate fruits were collected from the local market.

Fruit skins were rinsed with distilled water several times, dried in oven at 60°C and ground to fine powder in a kitchen grinder. 10 g the powder was extracted with 25 ml boiled distilled water at room temperature for 1 h. The clear extract obtained was centrifuged at 5000 rpm for 10 min at 5°C [26]. After the completion of extraction process, the extract was dried in oven at 50°C.

In this experiment iron oxide nanoparticles were synthesized by the co-precipitation process with some modification of the method described elsewhere [27]. Briefly, iron chloride hexahydrateate solution was mixed with another equal amount of iron sulfate heptahydrate with a molar ratio 2:1. The mixture was drop wise in 25 ml ammonium solution with stirring. The mixture was immediately became black which indicated the formation of iron oxide mixture was stirred for 15 min at 40°C. 0.1 g from Pom was dissolved in 10 ml of Mill-Q water was added to the mixture with stirring for 1 h at 60°C. The mixture was left to cool at room temperature and the resultant sample was denoted by the sample S1. The experiment was repeated with adding 0.2, 0.8 and 1.2 g of Pom were dissolved in 10 ml of deionized distal water to prepare the samples S2, S3 and S4 respectively. The samples were dried under vacuum for the measurements.

Characterization of the prepared samples

Transmittances Electron Microscope (TEM) image of samples were taken by JEOL JEM-2100 electron microscope. A drop of dried samples dispersed in ethyl alcohol was loaded on a grid and left to dry before measurement. The Fourier Transform Infrared (FTIR) spectra of the samples were recorded by Burker FTIR (VERTEX 70/80) spectrometer. Magnetic properties were measured through Vibrating Sample Magnometer (VSM) Lake shore 7410 USA. X-Pert panalatical X-ray Diffraction (XRD) device with CuKα 40kV/30mA was used for recording the X- ray diffraction pattern of the sample.

Application for dyes adsorption

The sample S3 is tested for the adsorption of dyes according to the method described in [28**]**. Briefly, stock solutions from methylene blue and red violet dyes were prepared by dissolving 50 mg in 1 liter of mill Q water. In polyethylene tubes 50 mg, 40 mg, 25 mg and 12.5 mg from the sample S3 was add to 5 ml of 10% H_2O_2 and 45 ml of 50 mg/l dye solution. The mixtures were shaken for 20 min at room temperature. The adsorbent particles were separated from the mixture by magnet. UV-Visible measured the peak at 665 nm for methylene blue and at 563 nm for red violet dye. This test was repeated at pH 5.3 and 6.8 for MB and at pH 5.4 and 6.3 for RV. Percentage of adsorption efficiency (A%) was calculated from the following Equation:

$$A\% = \frac{Co-Ce}{Co}\ 100$$

Where, Co is the initial and Ce is the equilibrium dye concentrations.

RESULTS AND DISCUSSION

TEM measurements

Figure 1 shows TEM image of S1, S2, S3 and S4. It is observed from Figure 1 that the particles size of S1 are in range 4.33-12.5 nm, S2 are 3.8-10 nm, S3 are 3.3-12.55 nm and S4 are 2.43-18.9 nm. These results indicated that Pom has no effect on the particle size of the formed Fe_3O_4.

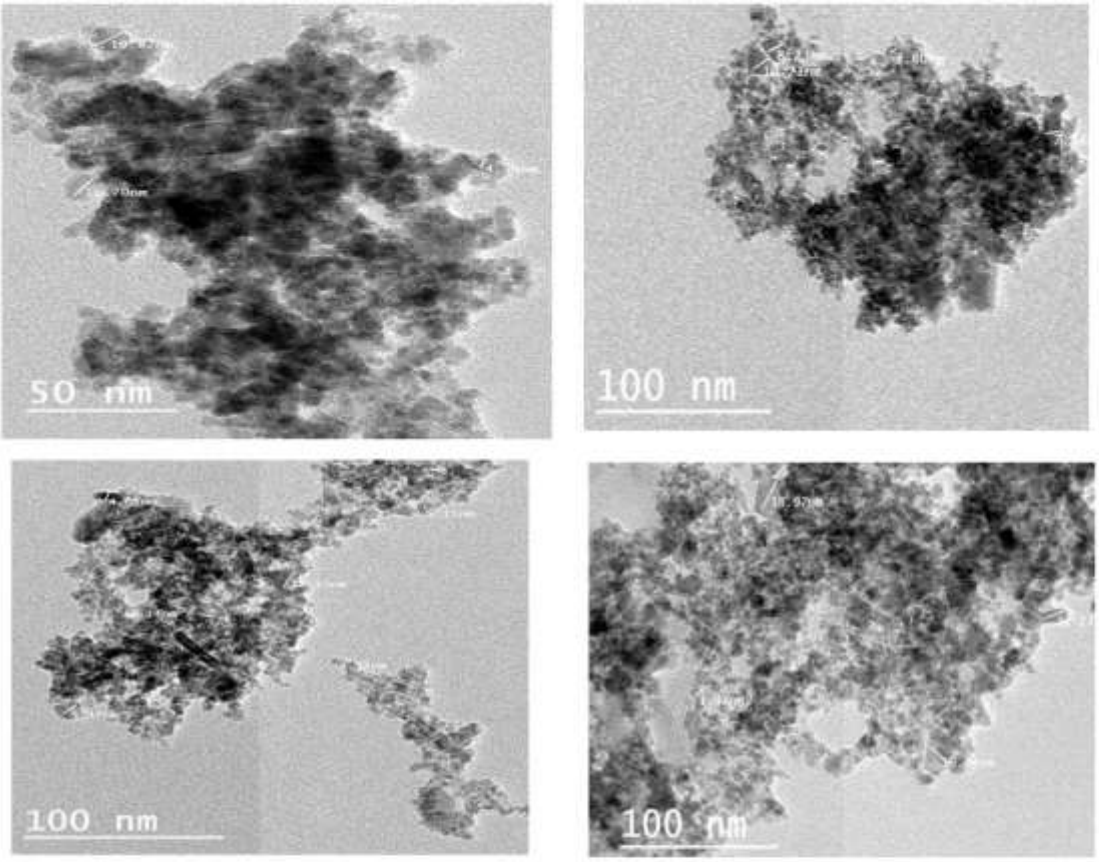

Figure 1: TEM image of samples S1, S2, S3 and S4

FTIR spectra

The FTIR spectra of S1, S2, S3, S4 and Pom are shown in Figure 2. It is observed that the Pom spectra has a bands at 3278 cm^{-1}, 2928 cm^{-1} which represent OH stretching vibration, C-H stretching of CH_2 bond respectively. The bands at 1720 cm^{-1}, 1600 cm^{-1} are assigned to C=O stretching vibration. The observed bands at 1343 cm^{-1}, 1238 cm^{-1} and at 1023 cm^{-1} are corresponding to the bending vibration of C-H bond in methyl groups, bending vibration of O-H and stretching vibration of C-O of carboxylic acids respectively.

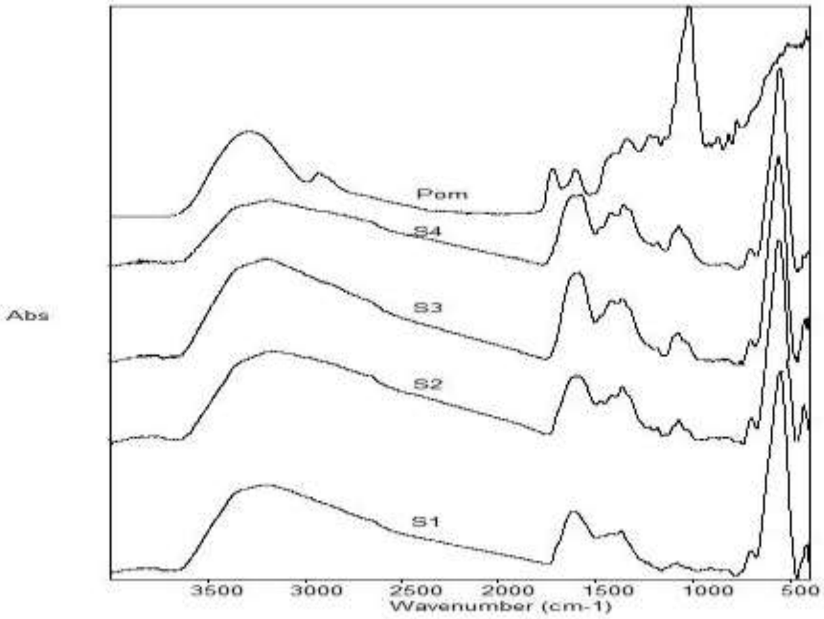

Figure 2: FTIR spectrum of Pom, S1, S2, S3 and S4

Comparing Pom spectra with S1, S2, S3 and S4 it is noticed that the disappearance of the bands at 1720 cm^{-1} and 1023 cm^{-1}, the shift in the band at 1600 cm^{-1} to 1617 cm^{-1} and the appearance of new bands at 1071 cm^{-1} in the spectra of S1, S2, S3 and S4. Also the appearance of the two characteristic bands of Fe_3O_4 at 583 and 443 cm^{-1}. These results indicated that the formed Fe_3O_4 is reacted with Pom through O of CO bond.

Magnetic properties

The hysteresis of S1, S2, S3 and S4 are representing in Figure 3. The magnetic properties of prepared nanoparticles were collected in Table 1.

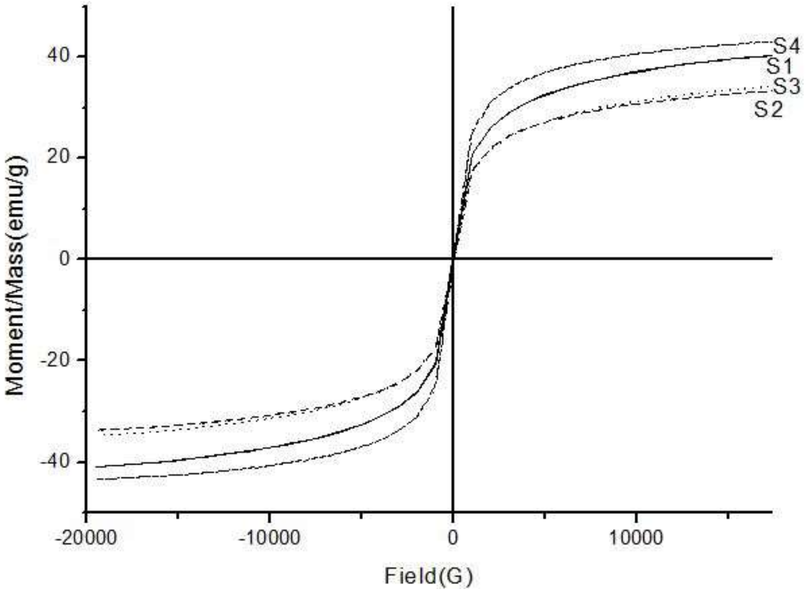

Figure 3: The hysteresis of S1, S2, S3 and S4

Table 1: The magnetic properties of prepared nanoparticles

	S1	S2	S3	S4
Hc G	22.853	41.882	27.839	38.91
Retentively (Mr) emu/g	0.67705	0.7776	0.59387	0.96375
Ms emu/g	40.033	33.67	34.6	43.31

Table 1 illustrated that the magnetic properties of all samples have values near to each other. The saturation magnetization for all prepared samples are lowest than that of bulk magnetite (98 emu/g^{-1}) [29]. The lowering in saturation magnetization can be attributed to the reduction of the particles sizes and Pom coated on the surface of Fe_3O_4 nanoparticles which acts as non-magnetic layer. In addition the samples have low coercively (Hc) and retentively (Mr). These results indicate that these prepared particles are in nano sizes and have super paramagnetic behavior.

XRD spectra

The XRD patterns of S1, S2, S3 and S4 are drowning in Figure 4. It is apparent that the diffraction pattern of the four prepared samples have the characteristic diffraction peaks at 2ϴ=30.2º, 35.5 º, 43.2º, 53.6º, 57.2º and 62.8º which are matched well with that of standard Fe_3O_4 crystalline magnetite (card no. 00-003-0863). These informed that the different concentration of Pom has no effect on the crystallinity of synthesis Fe_3O_4.

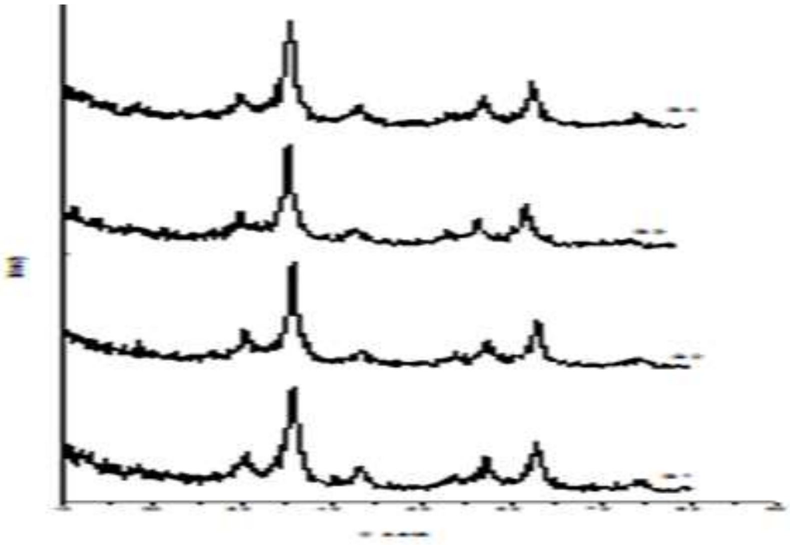

Figure 4: X-ray diffraction patterns of S1, S2, S3 and S4

Application of the prepared sample for dye adsorption

Figure 5 illustrate the relation between the concentration of adsorbent (Sample S3) and the percentage of adsorption efficiency to MB at pH 5.3 and 6.8. From this relation, it is observed that the percentage of adsorption efficiency of the adsorbent to MB at pH 6.8 is higher than that at pH 5.3. This percentage increase as the concentration of adsorbent increase and it is reach its maximum at 50 mg.

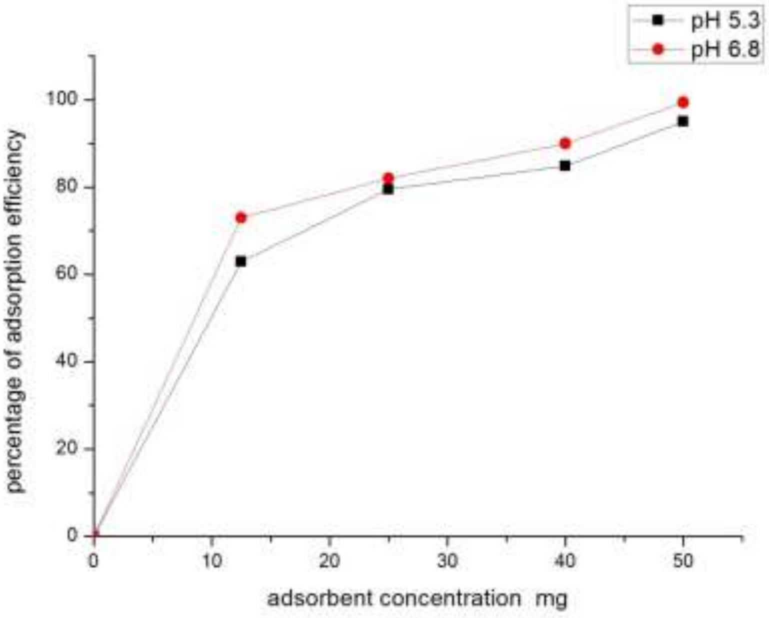

Figure 5: The relation between percentage of adsorption efficiency to removal of MB and the adsorbent concentration at pH 5.3 and 6.8

The relation between the concentration of adsorbent (Sample S3) and the percentage of adsorption efficiency for removal of RV at pH 5.4 and 6.3 is plotted in Figure 6. This relation shows that as the concentration of the adsorbent increase the percentage of adsorption efficiency increase in case of the two pH. At pH 6.3 the percentage of adsorption efficiency for removal of RV is higher than that at pH 5.4. These results indicated that the prepared nanoparticles are a good adsorbent for removal of MB and RV from water.

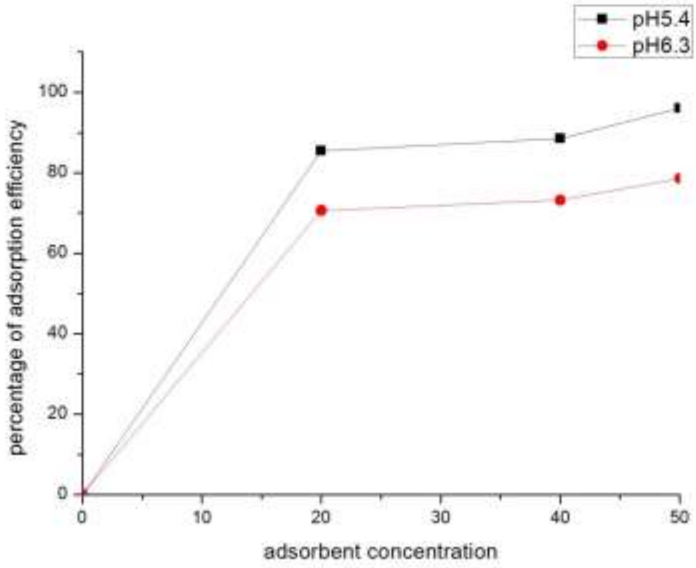

Figure 6: The relation between percentage of adsorption efficiency to removal of RV and the adsorbent concentration at pH 5.4 and 6.3

CONCLUSION

Iron oxide (magnetite) nanoparticles during were synthesis by co-precipitation method with addition of different amounts of pomegranate (*Punica granatum*) peel water extract as antioxidant and stabilizer. FTIR results determined that the formed iron oxide particles are reacted through the oxygen bond of CO group of the pomegranate peel water extract. The results of VSM and TEM measurements show that the produced particles had super paramagnetic properties and their sizes were in the range 3-19 nm, respectively. The tested sample S3 of the prepared particles for removing of methylene blue and red violet dyes from water at pH 5.3 and 6.8 for MB and at pH 5.4 and 6.3 for RV was a good adsorbent for both dyes. It can be concluded the obtained particles are in nano-size and have a super paramagnetic behavior. Fe_3O_4 particles reacted with Pom through O of CO bond. Finally, these particles are suitable for removing of MB and RV from water.

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