Removal of heavy metals from medical wastewater by using green synthesis FeO nanoparticles and resin

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Abstract

Heavy metals are considered one of the most dangerous pollutants. They are known as metallic elements with a high atomic weight: lead (Pb), cadmium (Cd), iron (Fe), chromium (Cr), copper (Cu), zinc (Zn), manganese (Mn), and nickel. (Ni) and silver (Ag) which may harm organisms in low concentrations and which accumulate in the food chain. This study aims to removal heavy metal from medical wastewater by using green FeO nanoparticles synthesis and resin. The results appeared the smallest crystal size by X-ray diffractometer was 16.58nm for FeO green synthesis with *Punica granatum* . The surface morphology of green FeO NPs appeared by using AFM, the average grain size was 40.139 nm and the nanoparticles were almost spherical. The outcomes of treatment the physical and chemical factors, heavy metals and bacterial growth was found that the column of resins with green synthesis FeO nanoparticles , the column showed a high removal rate of heavy metals (99.8-99.9%),also calcium(98.6%) ,magnesium(98.7%), total hardness(98.7%), total suspended solids(93.1%), total dissolved solids(99.3%), turbidity(81.2%) and conductivity(99.1%). It was concluded in the current study efficiency FeO nanoparticles green synthesis with aqueous extract of *Punica granatum* in treatment of wastewater and increasing the efficiency resin in treatment.

Keywords : Heavy metal , *Punica granatum*,FeO nanoparticles ,Resin

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Introduction

The wastewater for hospitals contains a wide range of toxic organic substances such as solvents, radioactive substances, pharmaceuticals, and disinfectants used for medical purposes in a wide range of concentrations. The association of hospital pollutants with aquatic ecosystems leads to risks directly related to the presence of hazardous substances, which have a negative impact on the balance the biological of environment. Pollution from medical wastewater can have an impact even at low concentrations. Aquatic organisms respond negatively to minimal concentrations of formaldehyde, one of the pollutants found in hospital wastewater. The presence of organochlorine complexes in high concentrations in hospital effluents has toxic effects on aquatic life(Kajitvichyanukul and Suntronvipart, 2006). Heavy metals are considered one of the most dangerous pollutants. They are known as metallic elements with a high atomic weight: lead (Pb), cadmium (Cd), iron (Fe), chromium (Cr), copper (Cu), zinc (Zn), manganese (Mn), and nickel. (Ni) and silver (Ag) which may harm organisms in low concentrations and which accumulate in the food chain. It is known that exposure to compounds containing toxic heavy metals that are known to be toxic, may cause genetic mutations, and are carcinogenic to humans (García-Niño and Pedraza-Chaverrí, 2014). Heavy metals are known to be one of the most persistent pollutants in wastewater. The release of large quantities of minerals into water bodies leads to serious health and environmental problems and may lead to an increase in wastewater treatment costs, and their appearance and accumulation in the environment are due to direct or indirect human activities. The stability of heavy metals in wastewater is due to their toxic and non-degradable nature (Akpor *et al.*, 2014). Several applications of water treatment have been used, as advanced water treatment is important for the efficient reuse of water resources. Several treatments with ion exchange resins and activated carbon are proposed to remove various pollutants in water, and a fixed bed column of pre-cured base ion exchange resin, acid ion exchange resin, mixed ion exchange resins, and modified activated carbon is applied to remove ionic pollutants and organic pollutants and adjust the pH value of the resulting water (Li *et al.,*, 2021).The applications of nanomaterials in water and wastewater treatment have received wide attention. Due to their small sizes, nanomaterials have strong adsorption and reactivity capabilities. Moreover, the high efficiency of nanomaterials transmission in solution. In addition, the high efficiency in removing heavy metals, organic pollutants, inorganic anions, and bacteria by different types of nanomaterials (Lu *et al.,*, 2016). In the modern era, there is a growing demand for the use of herbal extracts, particularly those arising from plant by-products, with effective use in food preservation, agriculture, medicine, and cosmetics, and in the treatment of water contaminated with dyes (Munekata *et al.,*,2020; Vidovix *et al.,*, 2021). Pomegranate peels *(Punica granatum*) make up nearly half the weight of the fruit and are not consumed directly and are disposed of as waste. The peels are rich in bioactive compounds, such as flavonoids, proanthocyanidins, hydrolyzable tannins polyphenols, compared to pomegranate juice and seeds (Gullon *et al.,*, 2016; Jalili *et al.,*, 2020). This study aims to removal heavy metal from medical wastewater by using green FeO nanoparticles synthesis and resin.

Methods

Samples collection from study area

Three sites were chosen to collect samples from the Tigris River near the city of medicine during four seasons (fall, winter, spring, and summer) (Figure1). The first point was located 700 m before the Medical City complex and the second was at the Medical City sewage discharge point into the river. The third point was located 1,300 meters from the drain point. The study was conducted from January to June 2021. Samples were taken at a depth of 10 cm to 30 cm below the surface of the water. Samples were collected between 7 AM and 8 AM during the pumps were running, and one sample was taken per site for each month. Sterile plastic bottles with a volume of 1.5 liters were used when collecting samples. Conductivity, pH, and temperature tests were performed locally on the same day of sample collection to avoid change. The samples were kept at a temperature of 4 degrees Celsius in order to preserve the characteristics of wastewater to study its treatment with nanoparticles in the laboratory. The wastewater treatment process included filtering the samples using 0.45μm pore filter paper and treating the filtered waste water by adding 1 ml of nitric acid to 50 ml of filtered water.

Figure (1) shows the sampling sites from the Tigris River to the Medical City

Measurement physical characteristic

It measured temperature, EC , turbidity using digital portable water meters, whereas TSS measured according (APHA,1999).

Measurement chemical characteristic

It measured pH using pH meter , TDS according (APHA,2005) ,total hardness (WHO,2003), Ca^{+2} and Mg^{+2} hardness(APHA,1985; APHA,1999).

Heavy metal measurement

The collected samples were analysed to measure the concentrations of heavy metals (lead, cadmium, iron and copper) in the laboratory by Flame atomic absorption spectrophotometer (SensAASGBC Scientific Equipment Dual /Australia). The analysis was performed according to the standard water and wastewater examination methods of the American Water Works Association, Water Environment Federation (APHA, 2002).

Total bacteria count

Wastewater was cultured to observe bacterial growth. The Petri dishes pouring method was adopted to count the total bacteria in the contaminated water (APHA, 1995).

Resin preparation

AMBERLITE IR120 Na resin is a strong acidic cationic (cationic) gel resin (sulfonated polystyrene) gel that has been used for water purification as well as for demineralization. AMBERLITE IR120 Na resin is an excellent ion exchange resin that can be widely used in a wide variety of applications Industrial water treatment, including both water purification and demineralization, is prepared from this type of resin (Kocaba, 2007). The raw water has been polluted with a concentration of 10 mg/ml each of (lead, cadmium, copper and iron) to test the optimum treatment of heavy metals.

Plant extract and preparation of FeO nanoparticles

Punica granatum extract was prepared by dissolving 20 g of pomegranate peel powder in 200 ml of deionized water and then filtered through 0.45 micron filter papers (Bibi *et al.,*, 2019).The nanoparticles were prepared by dissolving 5 g of iron salts (Fe2SO3) in 250 ml of deionized water to prepare iron oxides FeO, where it was heated at a temperature of 60 ° C, then 25 ml of aqueous extract of pomegranate was gradually added every 15 minutes, and the black color appeared. The mixture was then left at room temperature with stirring by a magnetic stirrer plate for an hour, then the final product was collected in test tubes by centrifugation at 1200 rpm, then the test tubes were placed in an ultrasonic device and then washed with water Deionized, then placed in dishes and left to dry at 60 °C for 3 hours in the oven (Bibi *et al.,*, 2019).

Measurement nanoparticles

The structural, morphological and optical properties of the composite nanoparticles (FeO) were characterized by X-ray Diffraction Measurements (XRD) and Atomic Force Microscopy (AFM) instruments.

Reduction of heavy metals by using green biosynthesis (Ferrous Oxide Nanoparticles with *Punica granatum*)and resins

The column were prepared, that containing the mixture of green nanoparticles and resin (where the charged and pre-prepared resin column was used and the green nanoparticles were placed in the column), then the water contaminated with heavy metals(10mg/L) was passed in the column to conduct the treatment process and the flow rate was calculated every 10 ml for 2.28 minutes. The pH function is measured before placing the polluted water to be 7, and then the concentrations of heavy metals (lead, cadmium, copper, iron) were measured using an atomic spectrometer after conducting the treatment process, Also, previously the metal concentrations were measured before treatment. In addition, calcium and magnesium were measured by method as mentioned previously, in addition to conducting physical and chemical tests as previously mentioned. Contaminated water was cultured before treatment and after treatment to observe bacterial growth.

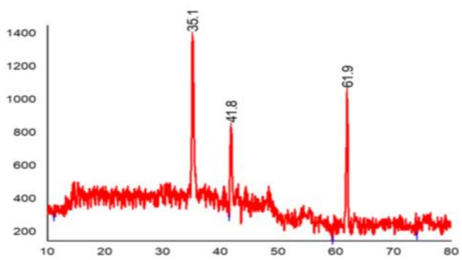
Results and discussion

Characterization of FeO nanoparticles

The X-ray diffractometer was used to examine the iron oxides synthesize with pomegranate peel extract to confirm the crystal system of the nanoparticles, where the diffraction angle θ2 was measured where three peaks were observed at θ2 which are 35.1110, 41.003, 61.9091 and their reflections were 110, 113, 214 respectively as in the table (1) and Figure (1), where the smallest value of the width of the half-maximum (FWHM) of the diffraction angle 2θ means the largest crystal size (Song *et al.,*, 2006), the crystal size of the fabricated nanoparticles for all peaks was also evaluated using Scherrer formula Scherer and the smallest crystal size was 16.58nm at a diffraction angle of 41.8003.

Table(1) Crystal size of iron oxide nanoparticles manufactured with pomegranate peel extract

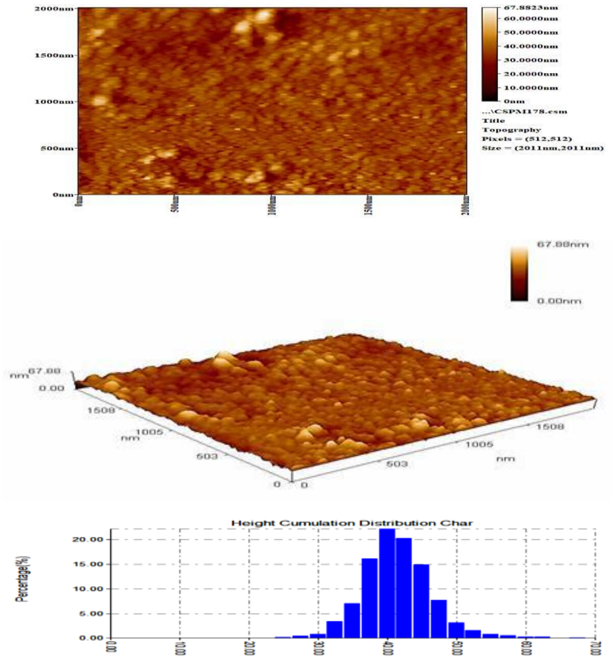
2θ(Deg.)	FWHM(Deg.)	Crystalline size D(nm)	hKl
35.1110	0.43430	18.30	110
41.8003	0.4797	16.58	113
61.9091	0.38421	20.6	214



Figure(1)XRD model of iron oxide nanoparticles manufactured with aqueous extract of pomegranate peels

Also, Mishra and Sardar (2015) showed that the diffraction angle peaks for iron oxide nanoparticles were 30.103,35.451, 43.088, 53.516, 56.998, 74.098,62.65 and their reflections were 220, 311, 400, 422, 511, 440, 533 for the surface of the cubic iron oxide nanoparticles. . Studies have shown that the use of plant extracts has important effects on the size and distribution of particles, as well as the shape, in addition to the use of plant extracts to produce nanoparticles in an excellent manner (Mohamad *et al.,*, 2014).

In this study surface morphology was studied using AFM images that produce surface topographic images at very high magnification. AFM images are widely known and provide a useful tool for describing the size and size distribution of nanoparticles. 2D and 3D AFM images are used to know the surface height, surface structure and accumulated distribution of iron oxide nanoparticles manufactured with pomegranate peels. AFM imaging was performed by drying FeO NPs solution on a clean glass plate. Average values were obtained, depending on the location of the measurements made on the samples. Figure (2) shows the surface morphology of preparing FeO NPs by the green method of pomegranate peel extract, the average grain size was 40.139 nm and it can be seen that the nanoparticles were almost spherical.In one study, it was observed that the particle size of iron oxide nanoparticles with pomegranate peel extract was variable and the maximum distribution was in the range of 28.4-66.2 nm (Bibi *et al.,*, 2019). This behaviour of nanoparticles was due to the presence of the envelope of different biologically active molecules (Mengistie *et al.,*, 2018 ; Friday *et al.,*, 2018), since the biologically active molecules have different functional groups, which interact with each other by interfacial forces and bonds). The presence of nanoparticles in aggregates is an indicator of strong intermolecular bonds, especially hydrogen bonds between hydroxyl groups and other bodies in the structure of the synthesis of phenolic compounds (Remya et al., 2017 ; Bibi *et al.,* 2017; Abebe *et al.,*, 2017).



Figue(2) Represents AFM images where (A) is a 2D image, (B) is a 3D image and (C) represents the granular distribution of iron oxide nanoparticles synthesized with pomegranate peel extract using green method.

Removal of heavy metal

Table (2) showed the outcomes of the physical and chemical factors, heavy metals and bacterial growth of the columns used in the treatment of polluted water, as it was found that the column of resins with green synthesis FeO nanoparticles , the column showed a high removal rate of heavy metals ,also calcium ,magnesium, total hardness, total suspended solids, total dissolved solids, turbidity and conductivity, moreover a decrease in bacterial growth was observed in the column of resins with green FeO nanoparticles as in Figure (3 and 4).

Table(2) The treatment water pollution with resin and green FeO nanoparticles

TH: Total hardness; TSS:Total solid suspended ; TDS: Total dissolve solid ; EC: electrical conductivity

Raw water	Concentration Mg/L	After precipitation	Concentration Mg/L	Treatment by green FeO with resin	Concentration Mg /L	Percentage removal %
Pb	0.25	Pb	10	Pb	0.02	99.8
Cd	0.026	Cd	10	Cd	0.02	99.8
Cu	0.25	Cu	10	Cu	0.01	99.9
Fe	1.32	Fe	10	Fe	0.01	99.9
Ca	510	Ca	380	Ca	5	98.6
Mg	700	Mg	565	Mg	7	98.7
TH	1210	TH	945	TH	12	98.7
TSS	225	TSS	190	TSS	13	93.1
TDS	2250	TDS	2200	TDS	14	99.3
Turbidity	56	Turbidity	16	Turbidity	3	81.2
EC	3700	EC	2108	EC	18	99.1
Temperature	25	Temperature	25	Temperature	25	25
pH	7.6	pH	7.4	pH	7.1	7.1
Bacterial growth	$2.8*10^7$	Bacterial growth	$2.8*10^7$	Bacterial growth	$1.88*10^6$	

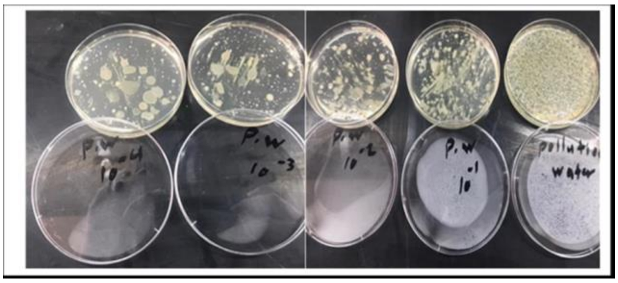


Figure (3) Bacterial growth in raw water pollution

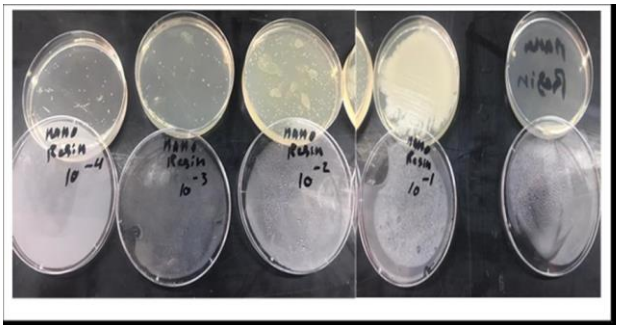


Figure (4) Bacterial growth after treatment by resin and green FeO nanoparticles

The application of the traditional ion exchange method is limited due to its low ability to absorb and wash away the effective functional groups. Thus, it is necessary to improve the adsorption capacity as well as the stability of ion exchange resins, while combining them with other effective adsorbents is promising for their use in water treatment (Raghuvanshib *et al.,*, 2017; Kim *et al.,*, 2009 Victor-Ortega *et al.,* ,2016). Some studies showed the efficiency of using nanoparticles in wastewater treatment. Where one of the studies showed the efficiency of FeO nanoparticles in removing pollutants, including arsenic, with a removal rate of 100% (Čižmar *et al.,*, 2020). Other studies showed the efficiency of FeO nanoparticles in removing chromium and cadmium with a 100% removal rate (Hao *et al.,*, 2014; Jerin. *et al.,*, 2019) and Lingamdinne *et al.,* (2020), when using iron oxide nanoparticles showed removal efficiency of 95% to lead.

Iron nanoparticles were also used to remove types of bacteria, including gram-positive bacteria such as Bacillus subtilis and gram-negative Pseudomonas, as well as types of fungi Aspergillus (Diao *et al.,*, 2009) . Iron oxide nanoparticles reduce oxidation processes. Therefore, there has been much interest towards iron oxide nanoparticles because they are known as non-toxic and biocompatible materials due to the presence of iron (II/III) ions (Leung *et al.,*, 2014) .A review of global studies showed a lack of studies in the use of green manufacturing of nano iron oxides with pomegranate peel extract in the treatment of heavy metals and biological pollution of wastewater, as it was not used by researchers except for one study conducted by Salmani *et al.,* (2021) who used Green manufacturing of iron oxides nanoparticles with pomegranate peel extract in removing arsenic, where the rate of removal speed was proven 20-60 minutes and thus proved its efficiency in removal.

Conclusions

It was concluded in the current study efficiency FeO nanoparticles green synthesis with aqueous extract of *Punica granatum* in treatment of wastewater and increasing the efficiency resin in treatment .

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