Synthesis of Iron Nanoparticles with Polyphenols Recovered from Olive Mill Wastewater and Their Use In Wastewater Treatment

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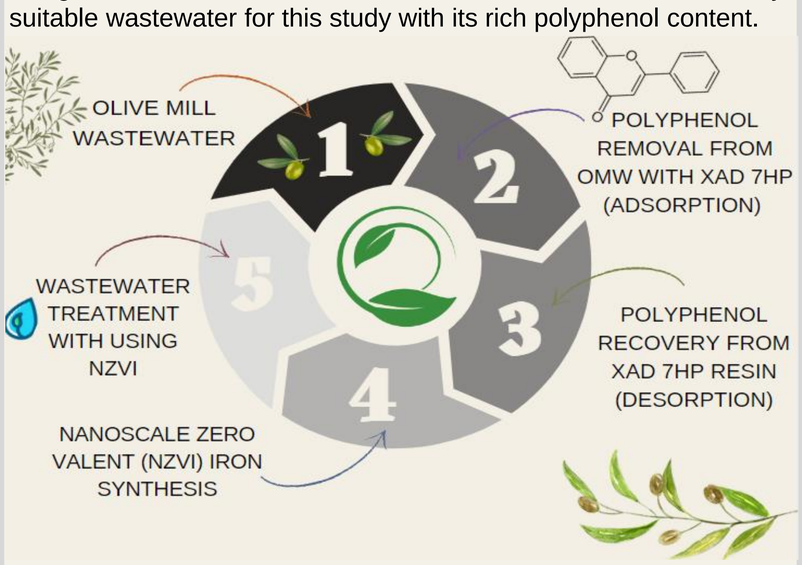
Introduction

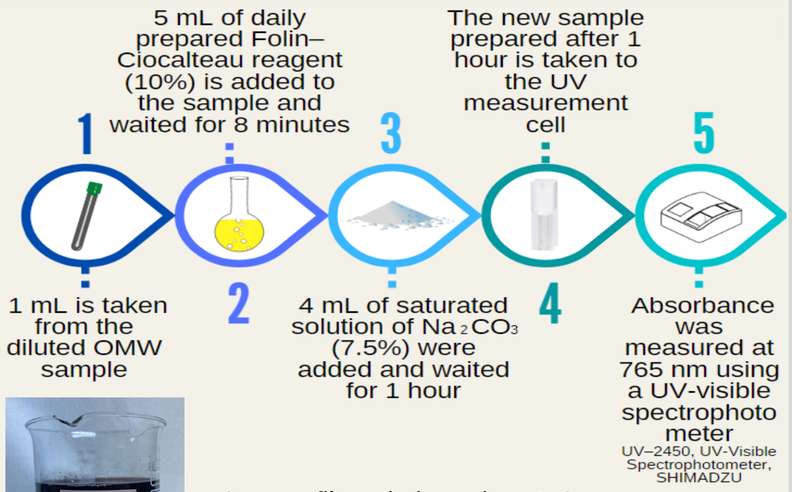
The green synthesis method is a safe, environmentally friendly and economical method since it does not contain harmful and toxic compounds in terms of inputs and products and is made with single-step renewable raw materials. The polyphenol in herbal extracts is a strong antioxidant and has the potential to react with metal solutions and form nanoparticles. The most important aspect of polyphenol for nanoparticle synthesis is that it is both a green reducing agent and prevents particles from aggregating without using an additional stabilizer. Olive mill wastewater is a very suitable wastewater for this study with its rich polyphenol content.

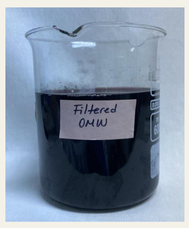


In this study, adsorption and desorption are used for recovery of polyphenols. In the trials, XAD 7HP resin was preferred over FPX66 resin due to its recovery efficiency and ease of application. Iron nanoparticle synthesis was carried out by varying the reaction pH, time and Iron/OMW (olive mill wastewater) volumetric ratio. The zeta potential and size/size distribution of the synthesized particles were compared. We propose that the recovery and use of polyphenols from olive mill effluent can contribute to the circular economy by harnessing a stream known as waste into a valuable product.

Materials&Methods

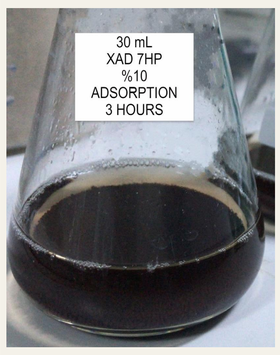
TPC (TOTAL PHENOL CONTENT) MEASUREMENT





- It was filtered through AP40 (0.7 µm pore size) filter.

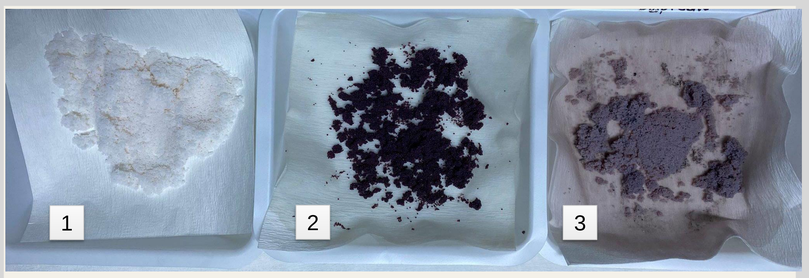
Adsorption Process For Removal Of Polyphenol from OMW



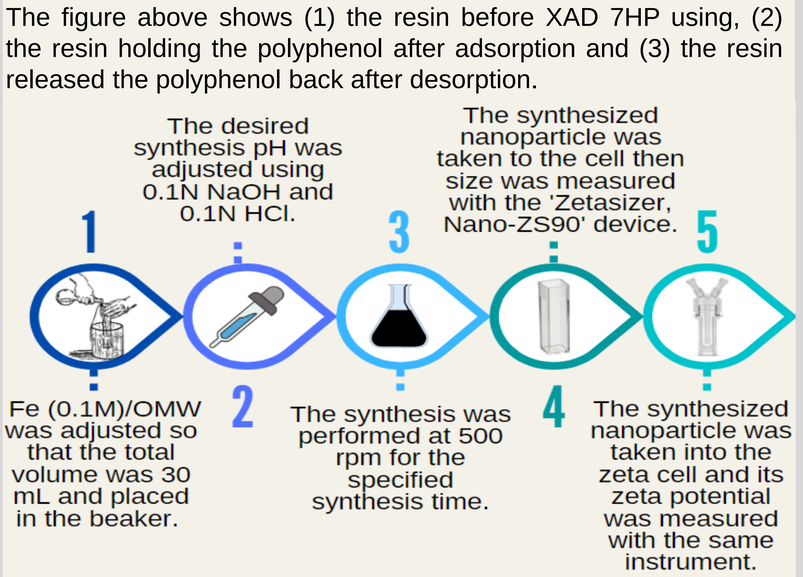
- OMW volume was taken as 30 mL.
- Resin volume was taken as 10% (3 g)
- 1 hour and 3 hours samples was taken for TPC measurement.
- After 3 hours, the resin was washed once with the sample and once with ultrapure water, centrifuged at 6000 rpm for 5 minutes and separated.

Desorption Process For Recovery Of Polyphenol from XAD 7HP

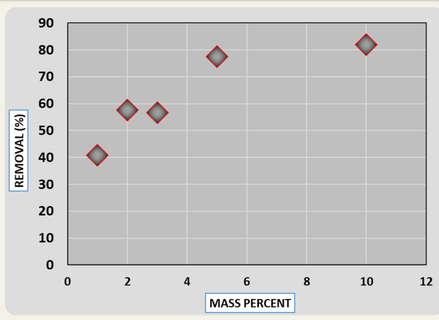
- After adsorption, resin was mixed with acidified ethanol (5%) solution and the desorption process was started.
- Samples were taken at 1 and 3 hours.
- Measured with the TPC method.
- After 3 hours, the released polyphenol was separated from the resin by using centrifuge.

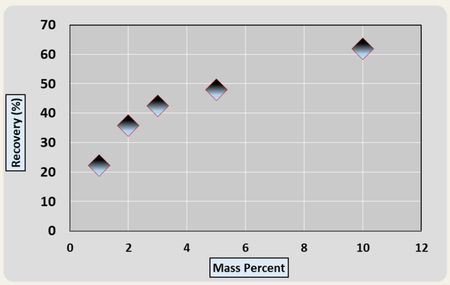


The figure above shows (1) the resin before XAD 7HP using, (2) the resin holding the polyphenol after adsorption and (3) the resin released the polyphenol back after desorption.



Results&Discussions





As a result of the experiments, it is possible to say that the following results have been achieved for nanoparticle synthesis.

1) When evaluated in terms of synthesis time, smaller sized iron nanoparticles were obtained with 20-minute synthesis compared to 60-minute synthesis. The measured size of the particles synthesized at the same concentration and pH in the synthesis time of 60 minutes were higher.

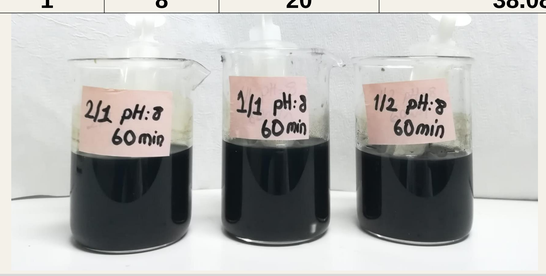
Fe	OMW	pH	Time (min)	Minimum Size (nm)
2	1	8	20	38.08
2	1	8	60	163.1

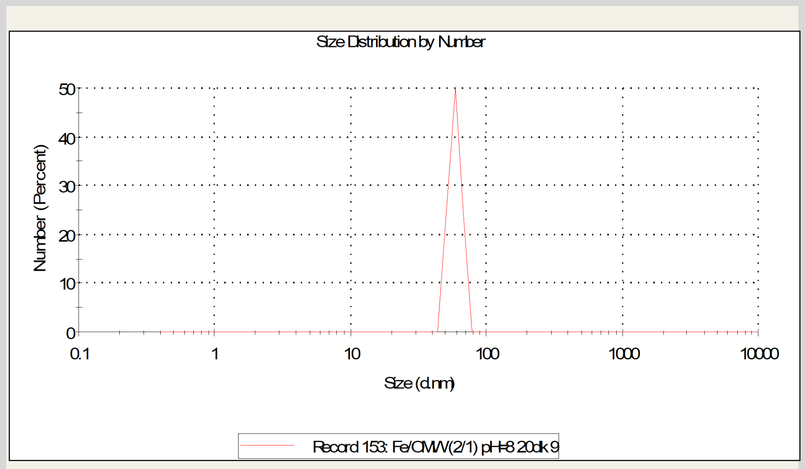
2) When iron nanoparticles synthesized at 4, 6 and 8 pH at the same concentration and synthesis time were examined, it was observed that iron nanoparticles synthesized at high pH were more stable, therefore, the measured zeta potential values were greater than 25 mV in absolute value. As a result, it was observed that nanoparticles synthesized at high pH were more stable and away from the tendency to aggregate.

Fe	OMW	pH	Time (min)	Average Zeta (mV)
2	1	4	20	4.48
2	1	6	20	-3.122
2	1	8	20	-57.08

3) In the synthesis experiments, when the iron volume was higher than the OMW volume, smaller nanoparticles were obtained at constant pH and synthesis times. It is possible to say that the increased iron volume has a positive effect on the nanoparticle size.

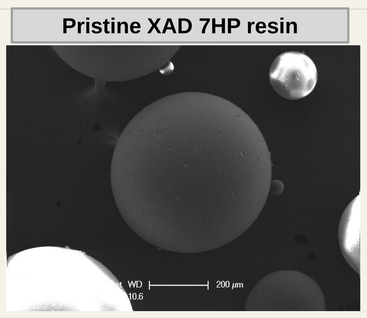
Fe	OMW	pH	Time (min)	Minimum Size (nm)
1	1	8	20	105.1
1	2	8	20	266
2	1	8	20	38.08



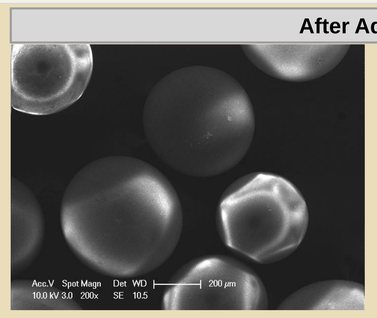


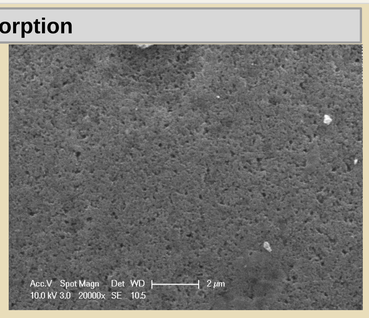
Characterization

Pristine XAD 7HP resin

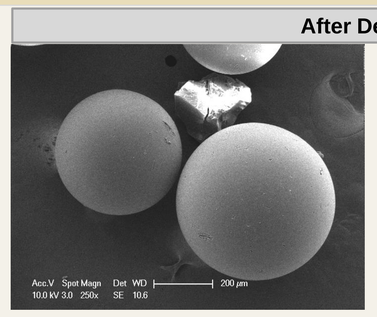


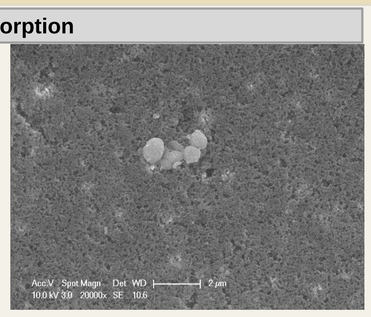
After Adsorption



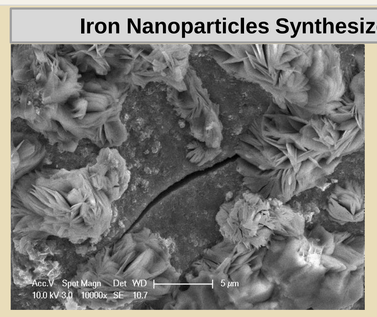


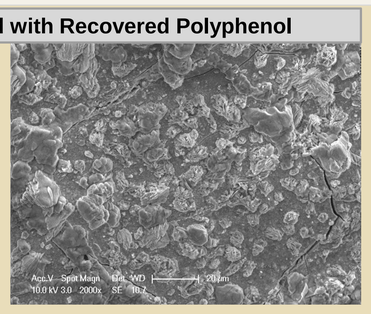
After Desorption





Iron Nanoparticles Synthesized with Recovered Polyphenol





Conclusion

1. In the study, an increase in polyphenol recovery and removal was observed when the percent by mass of the resin used was increased compared to OMW.

2. In line with all the results, considering both the zeta potential measurement and the size/size measurement of the nanoparticle; the nanoparticle synthesized with **2/1 (Fe/OMW)** at **8 pH** in **20 minutes;**

   ✓ Smaller nanoparticles (<100 nm)
   ✓ Higher zeta potential than 25mV in absolute value

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