# Synthesis and Characterization of Agar Coated Magnetic Iron Oxide Nanoparticles Prepared from Sand as Natural Iron Source for Removal of Ni ion from Aqueous Solution

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**Abstract**

Nickel is a hazardous metal that cause cancer and many other diseases. Agar coated magnetic iron oxide nanoparticles was investigated for the elimination of nickel from waste water. The magnetic nanoparticles were formed using a co-precipitation method from natural iron source. The nanoparticles have been described by a study of FT-IR, SEM, XRD and EDX. The FTIR outcomes confirmed that the iron oxide was successfully coated with agar while SEM results also indicated the coating of agar on iron oxide nanoparticles. The XRD pattern showed that bare magnetic particles were crystalline had sharp edges and spinal cube shape while the agar coated magnetic particles showed low crystallinity due to amorphous surface of agar. The EDX results revealed that about 76% iron is present in bare magnetic particles that decreased in agar coated nanoparticles, as prepared agar coated magnetic particles, the removal efficiency of Ni at optimum conditions was 89%.

## Introduction

Magnetic nanoparticles due to their unique properties and potential application in different areas such as magnetic separation, have drawn growing attention over past decades [1]. Magnetic particles such as maghemite ($Fe_2O_3$) and magnetite ($Fe_3O_4$) specifically magnetite commonly prepared by different preparation techniques such as co-precipitation [2], sol-gel reaction [3], hydrothermal [4], flow injection synthesis [5], polyol method [6], sonolysis [7], electrochemical method [8] and aerosol method [9], however, co-precipitation is undoubtedly the simplest and easiest way to prepare magnetic nanoparticles [10]. Iron oxides ($Fe_3O_4$ or $\pi Fe_2O_3$) are typically formed in aqueous medium by an aged stoichiometric combination of ferrous and ferric acid [11]. Nonetheless, apart from the Iron(II) and Iron(III) salts, the natural iron containing sand can also be used to synthesize magnetic nanoparticles. The synthesis of magnetic nanoparticles from natural iron-sand such as magnetite ($Fe_3O_4$) improves its financial value and boost potential uses like for biosensors, drug discovery, hypothermia, molecular imaging, bio-separation, computed tomography, bio-labeling, metal ion adsorption, *etc.* [12-20]. Nevertheless, their further implementation is limited due to tendency to aggregation. The modification or dispersion of magnetite in an appropriate matrix to avoid aggregation is therefore a new and good option [21]. Introduction of new substances could also introduce new magnetite feature. Agar, a polysaccharide, is commonly used in the nutrition and pharmaceutical companies, owing to its natural origin and economical price. Agars are cell membrane polysaccharides derived from marine red algae mainly consisting of alternating units *-(1-4)-d-galactose and -(1-3)-3,6-anhydro-L-galactose* continuous parts [22]. They are commonly used in the food industry as gel formers, thickeners, water holders, and stabilizers. Agar is also a clever, right matrix for the manufacture of magnetic nanoparticles, as this type of material has low cytotoxicity, elevated surface area, big pores, and temperature sensitivity, as well as biocompatibility and biodegradability [23].

Rupture of toxic substances in industrial effluents has now become a major problem in recent years, and has been regulated in almost every country due to its possible threat to humanity, health, and the atmosphere [24]. Regular wastewater treatment strategies include precipitation, ion exchange, and adsorption [25-28]. In addition to the adsorbing of aqueous solution metal ions, the magnetic adsorbent can be easily isolated from the solution. Therefore, synthesizing some novel magnetic adsorbents is still essential and important to encourage their applications in the region of ion adsorption.

In this research, we are going to explore the first-time preparation of agar coated magnetic iron oxide nanoparticles and its prospective implementation in solution adsorption of nickel ions. Prepared agar coated magnetic nanoparticles formulated from natural iron source using a co-precipitation method characterized by electron scanning microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Energy-dispersive X-ray (EDX), Spectroscopy, and X-ray diffractometer (XRD). In addition, the concentration of nickel ion removal under optimum conditions was also studied.

### Experimental section

**Materials:** Hydrochloric acid (37%, Merck), Sodium hydroxide (analytical grade, Merck), Agar (Fisher Scientific), Ethanol (analytical grade, Fisher Scientific), Dimethylglyoxime (analytical grade, Sigma-Aldrich), Iodine solution (analytical grade, Sigma-Aldrich), Ammonia (25%, Synth), Citric acid monohydrate (laboratory grade, Vetec) were obtained and used without any further purification.

**Preparation of nanoparticles:** As we reported in our previous work, the natural iron sand was obtained and treated with HCl at 100ºC for 80 minutes in nitrogen environment at constant stirring [27]. The solution was filtered and treated in two conditions: without agar solution marked as A and with 5% agar solution marked as B and heated at 100ºC was stirred for 15 minutes. NaOH solution was added to both solutions until pH reached at 11, a black precipitate was appeared which was filtered and washed several times with deionized water and ethanol to maintain pH 7, dried it at 120ºC for 24 h in an oven without air, until $Fe_3O_4$ nanoparticles powder was obtained as shown in Figure 1.



**Figure 1:** Magnetic nanoparticles showing magnetic properties.

**Characterization of prepared magnetic particles:** The data of sample were reported by x-ray diffraction (XRD) JDX-3532; JOEL, Japanof Cu Kα radiation (λ=1.544 nm) range at 20-70º (2ө) at 45 kV and 40 mA. Scanning electron microscope data was collected on JSM5910; JOEL, Japan) was used to characterize the morphologies. Fourier-transform infrared (FTIR) spectra were generated to confirm the existence of functional groups using model (Perkin-Elmer Spectrum 100) FTIR spectrometer in the range of 400-4000 $cm^{-1}$. The concentration of Ni ions was determined using UV-Vis spectrophotometer.

**Adsorption study:** The batch adsorption experiments of Ni ion on agar-coated magnetic nanoparticles (MNPs) were conducted. Ni stock solution was prepared in one liter of distilled water by dissolving 4.478 grams of $NiSO_4 * 6H_2O$. Different concentration Ni solution from 20 to 200 ppm was prepared in 50 mL and different amount of agar coated MNPs were added and stirred. The solution's pH had been balanced by using dil. HCl and NaOH. From the sample nanoparticles were separated by magnetic after equilibrium, and the filtrates were analyzed using the dimethylglyoxime (DMG) method by a UV-Visible spectrophotometry at 466 nm [29]. The equation below calculated the percentage removal of Ni ion.

% Removal of Ni ions = Co-Ce/Co x 100

Amount adsorbed in Ni ions (qe) = (Co-Ce)V/m

Where, Co and Ce are the initial and the final concentration of Ni (mg/L), m denoted the adsorbent mass (g), and V donated volume of the Ni solution (L).

### Result & discussion

**XRD characterization:** To confirm the presence of magnetic particle in agar, X-ray diffraction studies was carried out and Figure 2 shows the XRD patterns of bare magnetic nanoparticles as well as agar coated magnetic nanoparticles. The magnetic

nanoparticles diffraction activity is similar to the usual trend for spine-structured crystalline magnetite, which has peaks: (220), (311), (400), (511) and (440) [29,30]. Bare magnetic nanoparticles showed sharp peaks, while agar-coated magnetic nanoparticles have no sharp diffraction peaks. This is indication for amorphous materials and also for ultra-fine crystalline materials, where the peaks of diffraction cannot be well fixed. Therefore, it could be drawn that $Fe_3O_4$ magnetic nanoparticles with spinal structure in agar were embedded. The average crystal size was calculated from Scherrer equation and was 10.08 nm [31].
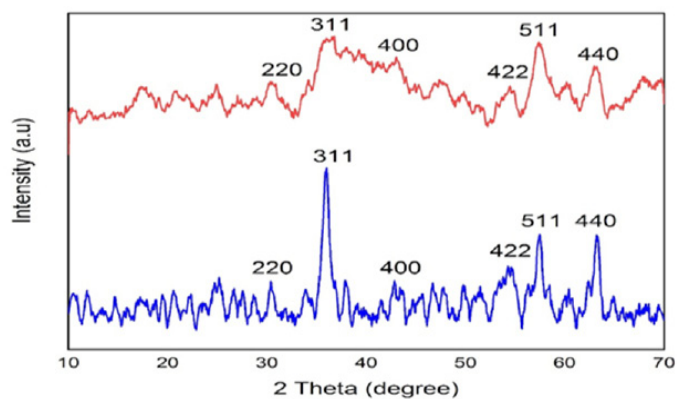


**Figure 2:** Showing XRD patterns of **(a)** bare nanoparticles and **(b)** agar coated nanoparticles.

**FT-IR characterization:** The Figure 3 shows the FTIR spectra of $Fe_3O_4$, agar and agar coated $Fe_3O_4$. The spectra confirm the conjugation of agar and $Fe_3O_4$ in the form of their functional group peaks. In (B) the $Fe_3O_4$ absorption band is 553 cm$^{-1}$ while the -OH group extension is due to the wide band at 3400 cm$^{-1}$. The standard absorption band in (A) is of agar. The peak of 1634 cm$^{-1}$ is the distinctive height of polysaccharides. The strong band between 840 cm-1 and 1225 cm$^{-1}$ refers to C-O stretching vibration while the highest at 3350 cm$^{-1}$ is due to -OH expansion. The value at 1034.66 cm$^{-1}$ reflects C-O-C and is assigned to the glycosidic bonding vibrational mode. The FT-IR spectra of agar-coated $Fe_3O_4$ revealed in (C), where the existence of magnetic nanoparticles peak at 554.86 cm$^{-1}$ (Fe-O) and also demonstrated the existence of agar peaks at 1030 cm$^{-1}$ (C-O-C) and 1634 cm$^{-1}$ related to agar, while on 3351 cm$^{-1}$ show expanding of -OH group, suggesting agar and magnetic nanoparticles conjugation [32].
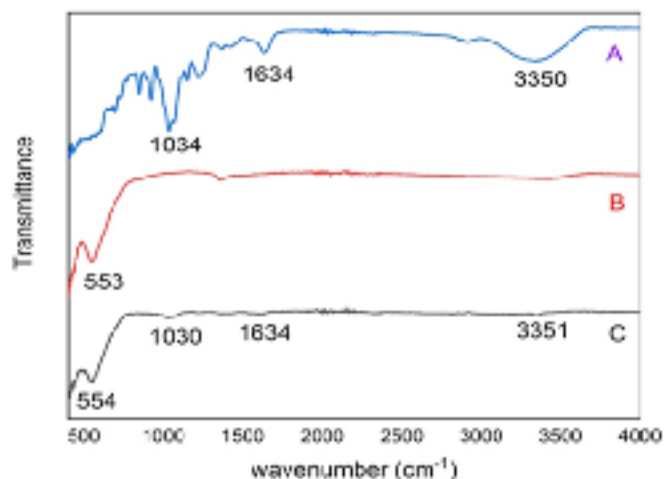


**Figure 3:** Shows FTIR spectra of **(a)** agar **(b)** $Fe_3O_4$ and **(c)** agar @$Fe_3O_4$.

**Morphological characterization:** The morphology of bare and agar coated $Fe_3O_4$ was determined by SEM. Figures A and B show the clear image of bare $Fe_3O_4$ while the Figures, C and D show agar coated $Fe_3O_4$. It can be seen from the images that the compositions of magnetic agar were significantly complicated. As seen from the pictures the size of particles increases after the coating of agar, second from A and B it is clearly seen that bared $Fe_3O_4$ was crystalline have sharp edges while from C and D the surface is smooth and look denser which indicate the confirmation of agar [33] (Figure 4).
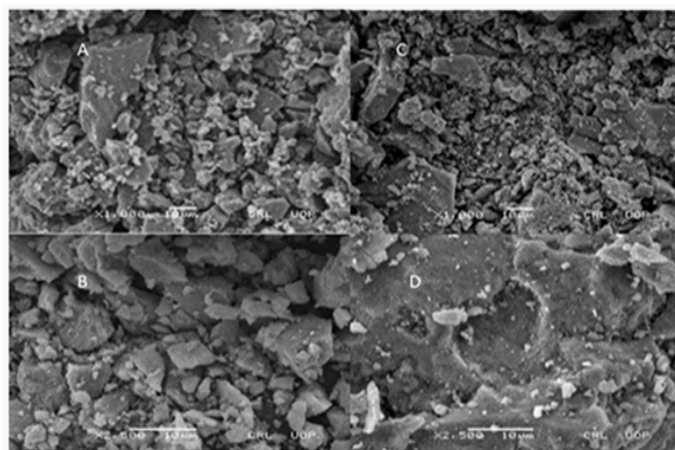


**Figure 4:** Shows SEM result of **(a,b)** $Fe_3O_4$ and **(c,d)** agar @$Fe_3O_4$.

**EDX characterization:** Comparison between EDX spectra of bare $Fe_3O_4$ and agar-coated $Fe_3O_4$ samples is seen in Figure 5 the peaks close to 0.3, 6.4 and 7 keV are correlated with bending Fe energy. In both spectra one peak is assign to Fe-O and one is for Fe while the Intensity of Carbon peak compared in both confirms the coating of Agar [34]. In case of elemental percentage in uncoated magnetic particles Fe are present 76.71% while Carbon is 1.75%. in coated magnetic particles Fe are present 75.58% while Carbon is 5.49% which also indicates the coating of agar and its magnetic properties.



**Figure 5:** EDX result of **(a)** bare $Fe_3O_4$ and **(b)** agar coated $Fe_3O_4$.

**Adsorption study**

**Effect of adsorbent dosage:** The experiments were carried out at room temperature from 1 to 10 g/L at pH 7 to calculate the adsorbent concentration's effect on the adsorption of nickel from aqueous solution. The percentage removal of nickel metal on agar coated magnetic particles is reflected in the results of the adsorbent dose as shown in Figure 6.1. Initially, the metal absorption improved with an adsorbent dosage of 01g/L to 10g/L and achieved a balance of 6g/L. This is due to improved surface of adsorbent and extraavailable adsorption sites [35]. Based on these tests, 6g/L was used as the maximal adsorbent dosage for the remaining experiments.
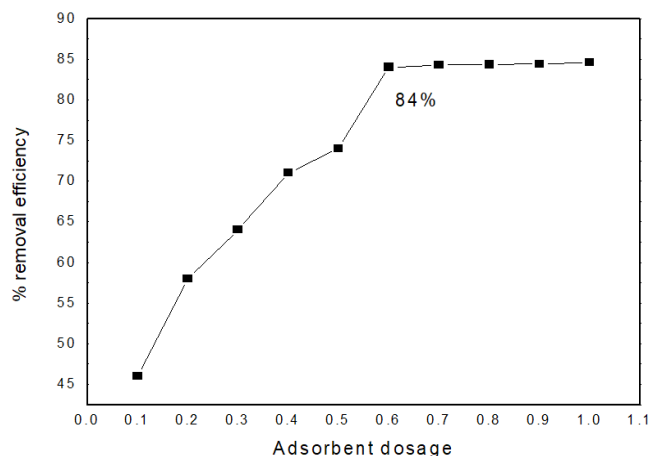
Figure 6.1: Shows graph between adsorbent dosage *vs* % removal efficiency of agar @ $Fe_3O_4$.

**The effect of pH:** pH's effect on the adsorption of nickel is expressed in Figure 6.2. The effect was tested at room temperature, initial concentration of metal 100mg/L, adsorbent dose 1g/L by varying the pH of metal solution from 2-10. With the increased pH the percentage of adsorption increases. Minimum adsorption was identified at low pH due to the adsorption locations were saturated by $H^+$ ions. Higher adsorption was recorded at pH raised between 6 to 8 as adsorption sites were available to Ni ions. The pH above 8 can make the metal to form its hydroxide as more hydroxyl ions are present [36]. It was evident from these tests that the highest metal absorption was taken at pH 7 *i.e.* 84.58 per cent based on this pH 7 has optimal pH for the rest of the experiments.
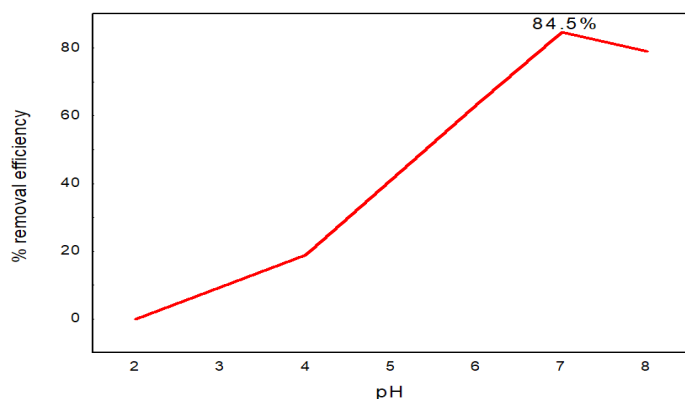


Figure 6.2: Shows graph between pH of solution *vs* % removal efficiency of agar @ $Fe_3O_4$.

**Effect of interaction time:** Interaction time of adsorbent with adsorbate is also having great effect on the adsorption on metal. For this, batch adsorption experiments were conducted between 30-150 min range. The metal ion concentration was 100mg/L, at the pH 7, and at room temperature, while the agar coated $Fe_3O_4$ addition was 6g/L, respectively. From Figure 6.3 the plot reveals that at the beginning the amount of nickel elimination was smaller. It may be due to less interaction time agar-coated $Fe_3O_4$ particles with nickel ions. Adsorption of the equilibrium was accomplished within a time of about 90 min suggesting that the adsorption sites are well defined [38]. For the results it is obvious that nickel adsorption depended on the time of interaction. Based on these findings, all the batch experiments with time of 90 min were performed.
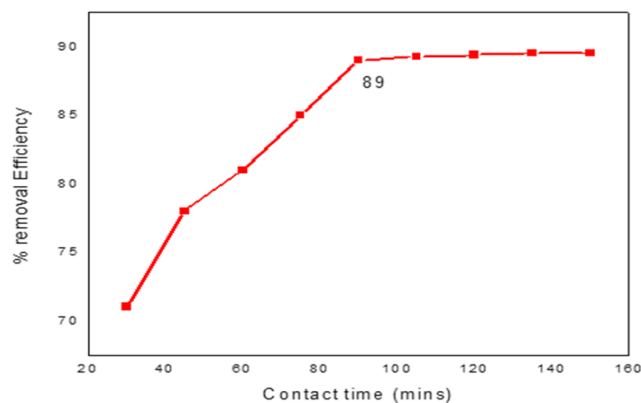


Figure 6.3: Shows graph between contact times of nanoparticles with Ni ions in solution *vs* % removal efficiency of agar @ $Fe_3O_4$.

## Conclusion

In this study, $Fe_3O_4$ magnetic agar composites were preparedusing natural iron sand as a source of Fe and using agar as a solid carrier. Two different samples were prepared, one bare $Fe_3O_4$ and the other is coated with agar. The characterization of both samples was examined by XRD, EDX, SEM and FT-IR. The result shows the conjugation of agar with $Fe_3O_4$ and also XRD result reveals that agar decrease the crystallinity of agar coated samples of iron nanoparticles. SEM, EDX and FT-IR confirmed the agar presence. Such nanoparticles have been also used to extract Ni ions from aqueous solution and gave findings of 89%.

Conflict of Interest statement: On behalf of all authors, the corresponding author states that there is no conflict of interest.

### References

1. Liu JF, Zhao ZS, Jiang GB. Coating Fe3O4 magnetic nanoparticles with humic acid for highly efficient removal of heavy metals in water. Environmental Science & Technology. 2008; 42: 6949-6954.

2. Li XW, Gupta A, Xiao G, Qian W, Dravid VP. Fabrication and properties of heteroepitaxial magnetite (Fe3O4) tunnel junctions. Applied Physics Letters. 1998; 73: 3282-3284.

3. Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L, Muller RN. Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. Chemical Reviews. 2008; 108: 2064-2110.

4. Dai Z, Meiser F, Möhwald H. Nanoengineering of iron oxide and iron oxide/silica hollow spheres by sequential layering combined with a sol–gel process. Journal of Colloid and Interface Science. 2005; 288: 298-300.

5. Hyeon T, Lee SS, Park J, Chung Y, Na HB. Synthesis of highly crystalline and monodisperse maghemitenano-crystallites without a size-selection process. Journal of the American Chemical Society. 2001; 123: 12798-12801.

6. Salazar-Alvarez G, Muhammed M, Zagorodni AA. Novel flow injection synthesis of iron oxide nanoparticles with narrow size distribution. Chemical Engineering Science. 2006; 61: 4625-4633.

7. Abd Elrahman AA, Mansour FR. Targeted magnetic iron oxide nanoparticles: Preparation, functionalization and biomedical application. Journal of Drug Delivery Science and Technology. 2019; 52: 702-712.

8. Anggraeni SD, Kurniawan F. Synthesis of Aluminium Nanoparticles Using Electrochemical Method. In Journal of Physics: Conference Series. 2020; 1445: 012013.

9. Laurent S, Boutry S, Mahieu I, Elst LV, Muller RN. Iron oxide-based MR contrast agents: from chemistry to cell labeling. Current Medicinal Chemistry. 2009; 16: 4712-4727.

10. Gonzalez-Carreno T, Morales MP, Gracia M, Serna CJ. Preparation of uniform γ-Fe2O3 particles with nanometer size by spray pyrolysis. Materials Letters. 1993; 18: 151-155.

11. Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L, Muller RN. Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. Chemical Reviews. 2008; 108: 2064-2110.

12. Laurent S, Forge D, Port M, Roch A, Robic C, et al. Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. Chemical Reviews. 2008; 108: 2064-2110.

13. Zhu S, Guo J, Dong J, Cui Z, Lu T, et al. Sonochemical fabrication of Fe3O4 nanoparticles on reduced graphene oxide for biosensors. UltrasonicsSonochemistry. 2013; 20: 872-880.

14. Cao SW, Zhu YJ, Ma MY, Li L, Zhang L. Hierarchically nanostructured magnetic hollow spheres of Fe3O4 and γ-Fe2O3: preparation and potential application in drug delivery. The Journal of Physical Chemistry C. 2008; 112: 1851-1856.

15. Qu J, Liu G, Wang Y, Hong R. Preparation of Fe3O4–chitosan nanoparticles used for hyperthermia. Advanced Powder Technology. 2010; 21: 461-467.

16. Lin LS, Cong ZX, Cao JB, Ke KM, Peng QL, et al. Multifunctional Fe3O4@ polydopamine core shell nanocomposites for intracellular mRNA detection and imaging-guided photothermal therapy. ACS Nano. 2014; 8: 3876-3883.

17. Adams SA, Hauser JL, Allen ALC, Lindquist KP, Ramirez AP, et al. Fe3O4@ SiO2 nanoparticles functionalized with gold and poly (vinylpyrrolidone) for bio-separation and sensing applications. ACS Applied Nano Materials. 2018; 1: 1406-1412.

18. Chen JS, Zhang Y, Lou XW. One-pot synthesis of uniform Fe3O4 nanospheres with carbon matrix support for improved lithium storage capabilities. ACS Applied Materials & Interfaces. 2011; 3: 3276-3279.

19. Hong RY, Feng B, Chen LL, Liu GH, Li HZ, et al. Synthesis, characterization and MRI application of dextran-coated Fe3O4 magnetic nanoparticles. Biochemical Engineering Journal. 2008; 42: 290-300.

20. Sun P, Zhang H, Liu C, Fang J, Wang M, Chen J, et al. Preparation and characterization of Fe3O4/CdTe magnetic/fluorescent nanocomposites and their applications in immuno-labeling and fluorescent imaging of cancer cells. Langmuir. 2009; 26: 1278-1284.

21. Ren Y, Abbood HA, He F, Peng H, Huang K. Magnetic EDTA-modified chitosan/SiO2/Fe3O4 adsorbent: preparation, characterization, and application in heavy metal adsorption. Chemical Engineering Journal. 2013; 226: 300-311.

22. Liu Y, Wang A, Claus RO. Layer-by-layer electrostatic self-assembly of nanoscale Fe3O4 particles and polyimide precursor on silicon and silica surfaces. Applied Physics Letters. 1997; 71: 2265-2267.

23. Araki C, Arai K. Studies on the chemical constitution of agar-agar. XXIV. Isolation of a new disaccharide as a reversion product from acidic hydrolysate. Bulletin of the Chemical Society of Japan. 1967; 40: 1452-1456.

24. Liu J, Chen L, Li L, Hu X, Cai Y. Steady-state fluorescence study on release of camptothecin from agar hydrogel. International Journal of Pharmaceutics. 2004; 287: 13-19.

25. Ahalya, N., Ramachandra, T. V., &Kanamadi, R. D. (2003). Biosorption of heavy metals. The Research Journal of Chemistry and Environment, 7(4), 71-79.

26. Pagnanelli F, Toro L, Veglio F. Olive mill solid residues as heavy metal sorbent material: a preliminary study. Waste Management. 2002; 22: 901-907.

27. Nasrullah S. "Synthesis and Characterization of Starch Coated Natural Magnetic Iron Oxide Nanoparticles for the Removal of Methyl Orange Dye from Water." 2021.

28. Khanzada A, Khalid N. "Removal of organic micropollutants using advanced membrane-based water and wastewater treatment: A review." Journal of membrane science. 2020; 598: 117672.

29. Hsieh S, Huang BY, Hsieh SL, Wu CC, Wu CH, et al. Green fabrication of agar-conjugated Fe3O4 magnetic nanoparticles. Nanotechnology. 2010; 21: 445601.

30. Es'haghi Z, Vafaeinezhad F, Hooshmand S. Green synthesis of magnetic iron nanoparticles coated by olive oil and verifying its efficiency in extraction of nickel from environmental samples via UV vis spectrophotometry. Process Safety and Environmental Protection2016; 102: 403-409.

31. Zhang F, Li X, He N, Li T, Sauli E. Novel Synthesis of Magnetic Agar and Its Application in Cu Ions Adsorption. Journal of Nanoscience and Nanotechnology. 2015; 15: 9721-9725.

32. Zhang F, Li X, He N, Li T, Sauli E. Novel Synthesis of Magnetic Agar and Its Application in Cu Ions Adsorption. Journal of Nanoscience and Nanotechnology. 2015; 15: 9721-9725.

33. Hsieh S, Huang BY, Hsieh SL, Wu CC, Wu CH, et al. Green fabrication of agar-conjugated Fe3O4 magnetic nanoparticles. Nanotechnology. 2010; 21: 445601.

34. Zhang F, Li X, He N, Li T, Sauli E. Novel Synthesis of Magnetic Agar and Its Application in Cu Ions Adsorption. Journal of Nanoscience and Nanotechnology. 2015; 15: 9721-9725.

35. Wulandari IO, Mardila VT, Santjojo DDH, Sabarudin A. Preparation and characterization of chitosan-coated Fe3O4 nanoparticles using ex-situ co-precipitation method and tripolyphosphate/sulphate as dual cross linkers. In IOP Conference Series: Materials Science and Engineering. 2018; 299: 012064.

36. El-Ashtoukhy ES, Amin NK, Abdelwahab O. Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. Desalination. 2008; 223: 162-173.

37. Orumwense FF. Removal of lead from water by adsorption on a kaolinitic clay. Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental and Clean Technology. 1996; 65: 363-369.

38. Mezenner NY, Bensmaili A. Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste. Chemical Engineering Journal. 2009; 147: 87-96.