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SCIENTIFIC PAPER

UDC

REMOVAL OF MANGANESE IONS USING Fe_2O_3 NANOPARTICLES IN PICKERING EMULSION LIQUID MEMBRANES

Highlights

- Ferric oxide nanoparticles (Fe_2O_3 NPs) were synthesized from human hair waste
- Fe_2O_3 NPs were characterized using SEM, XRD, and FTIR
- Fe_2O_3 NPs from human hair significantly improved Pickering emulsion liquid membranes (PELM)
- The maximum Mn(II) removal of 93.1% was achieved under optimal conditions

Abstract

The present investigation is directed toward obtaining ferric oxide nanoparticles (Fe_2O_3 NPs) from discarded human hair in an environmentally friendly way while at the same time examining the possibility of using them as Pickering stabilizers in emulsion liquid membranes (PELMs) for Mn(II) uptake removal from contaminated water. The synthesis of Fe_2O_3 NPs was done through a method involving hair extract-assisted sonochemistry, and it was confirmed by FTIR spectroscopy, X-ray diffraction, and microscopy that these nanoparticles have Fe and O characteristic stretching modes, a crystalline structure, and a very thin, flaky morphology. Based on sunflower oil (W/O/W) emulsion liquid membranes (PELMs) composed of Span 80, tributyl phosphate (TBP), and hydrochloric acid (HCl), their performance was studied under different conditions related to feed pH, initial Mn(II) concentration (5-25 mg/L), stirring speed (300-500 rpm), and HCl concentration (0.1-0.8 M). The manganese removal, together with membrane stability, mostly depended on the agitation or stirring rate and the acidity level of the stripping solution. At 400 rpm and 0.4 M HCl, about 93.1% of the initial Mn(II) was removed. The research has proven the great potential and advantages of hair-derived Fe_2O_3 NPs in heavy metal removal processes and in turning biowaste into valuable resources.

Keywords: human hair waste; ferric oxide nanoparticles; Pickering emulsion liquid membrane; manganese removal, waste valorization.

INTRODUCTION

Human hair represents a significant form of biowaste; due to its unique physicochemical properties, hair can be reused significantly in many ways, including but not limited to agriculture and fashion [1,2]. The resilient nature of keratin in human hair waste causes it to remain in the environment for extended durations, pointing to the urgent need for sustainable disposal methods. Recent experimental studies have shown that human hair fibers and millet husks can serve as effective substitutes, enhancing both the performance and eco-friendliness of concrete. This study applied human hair fibres (HHF) and millet husk ash (MHA) to take advantage of the synergy between MHA and HHF to improve durability, increase strength, and enhance overall performance. The research implemented a menu of solutions that will not only reduce waste but also save people money in making building materials. Beyond construction, research has validated a method to effectively isolate melanosomes from human hair waste, providing a yield of approximately 1.3%, as a percentage of total hair mass, of melanosomes and their structural integrity is importantly maintained [3]. The melanosomes maintain surface morphology and ultrastructure as shown by electron microscopy. Supplementing potato dextrose agar (PDA) with 100% v/v waste human hair broth (WHHB) substantially enhanced the growth of *Pleurotus ostreatus*. L., demonstrating the broth's high nutritional value. Human hair keratin contains the most cysteine of keratin-forming sources, and it is also a source that is able to absorb heavy

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metal ions, making human hair keratin (HHK) an effective and sustainable material with significant potential in mitigating ecological contaminants. Silver nanoparticles (AgNPs) were bound to HHK/poly-ethylene oxide (PEO)/ polyvinyl alcohol (PVA) mats and subsequently characterized. Electron microscopy with energy-dispersive X-ray spectroscopy (EDS) cor-roborated that the majority of the AgNPs were bound to the respective sulphur-containing amino acid residues of HHK, suggesting promising antibacterial and biocompatibility applications [4–7]. Nanotechnology encompasses a fortunate field of science that has made unprecedented advances in our modern world of technology. The biocompatible syn-thesis of nanoparticles is a major research area in nanotechno-logy [8]. In this research, we incorporated nanotechnology with keratin waste using a method to synthesize ferric oxide nanoparticles (Fe_2O_3 NPs) from human hair. The nanoparticles that we synthesized showed significant antioxidant activities. Other studies have demonstrated the ability to synthesize Fe_2O_3 NPs using vermicomposting leachate as well [9].

Fe_2O_3 NPs are metal oxide nanoparticles of great interest due to their advantageous characteristics, such as superparamagnetism, high reactivity, biodegradability, availability, and biocompatibility [10,11]. It has recently been reported that Fe_2O_3 NPs synthesized from iron chloride ($FeCl_3$) were tested for their viability as an efficient catalyst for Nitrocellulose without risk. We have already shown Fe_2O_3 NPs to be biosynthesized using aqueous leaf extract of *Ruellia tuberosa* L. [12-14]. Biosynthesized Fe_2O_3 NPs showed significant inhibitory activity against *Escherichia coli* and *Klebsiella pneumoniae*. The synthesized Fe_2O_3 NPs showed the ability to photo-catalytically degrade violet crystal dye when irradiated with a source of solar light, achieving up to 80% degradation.

Water pollution by manganese (Mn(II)) present in industrial and mining waste raises environmental concerns, demanding effective methods for water treatment. Precipitation, adsorption, and ion exchange have been used for water purification; however, such techniques have drawbacks associated with low selectivity, sludge production, and high costs. Among others, an alternative is a promising method based on emulsion liquid membrane technology, characterized by a high extraction rate and the possibility of simultaneous extraction and stripping. However, traditional ELMs utilize surfactant stabilizers that create problems associated with the instability, swelling, and leakage of the emulsions that affect the practical applicability of the method [6]. In the present study, a Pickering emulsion liquid membrane (PELM) refers to a water-in-oil-in-water (W/O/W) emulsion stabilized by Fe_2O_3 nanoparticles, which are located at the oil-water interface and form a rigid interface layer to improve the emulsion stability and thus avoid leakage and coalescence. Mn(II) ions are transported from the external feed phase through the membrane containing an organic phase with TBP as the carrier into the internal stripping phase. In this case, Fe_2O_3 nanoparticles were mainly used as Pickering stabilizers, while TBP was used as a carrier for Mn(II) transport.

PELMs, characterized by the use of nanoparticles as stabilizers, have drawn the interest of researchers recently. Nanoparticles, adsorbed irreversibly at the oil-water interface, create a rigid film, increasing the resistance to leakage and coalescence of droplets in PELMs. Generally, a double emulsion of the water-in-oil-in-water (W/O/W) type is produced. Thus, transport of Mn(II) ions is provided via diffusion and facilitated transport. Being more stable, having a larger interface area, and providing higher mass transfer rates, PELMs show high efficacy in water treatment and removal of heavy metals in particular [14].

The efficiency of PELMs depends significantly on a number of factors that determine not only the effectiveness of metal ion extraction but also the stability of the system itself. Among these factors, the pH of the feed solution serves as an important factor responsible for the speciation of metal ions and the nature of their interaction with the membrane interfaces [6,14]. The effect of the initial feed concentration is associated with the impact on the driving force of the process of metal ion transfer across the membrane interface. Moreover, the influence of the agitation rate can be traced due to its influence on the interfacial surface and size distribution of the dispersed phase particles [6]. Also, similar to the stripping agent concentration, which defines the efficiency of the metal ion removal from the internal phase, its concentration determines the degree of osmotic swelling and membrane breakage [14].

From several nanomaterials available, Fe_2O_3 NPs have gained great popularity owing to their large surface area, good stability, biocompatibility, and strong interfacial adsorption capacity [10,11]. The above-listed features of Fe_2O_3 NPs make them suitable stabilizers in Pickering emulsions, which help enhance the stability of membranes and improve extraction efficiency. Current research trends are highlighting the significance of green routes for nanoparticle synthesis that can contribute to minimizing the impact on the environment. Considering the above point, human hair waste, a biowaste material comprising keratin and about 67–88% protein content along with some functional groups, such as $-NH_2$, -COOH, and -SH, is one of the promising candidates for nanoparticle synthesis [1,3]. These biomolecules serve as natural reducers and stabilizers, making the eco-friendly synthesis of nanomaterials possible. While numerous studies have been conducted on Fe_2O_3 nanoparticles for environmental purposes as well as for catalytic applications [9,14], synthesis of such nanoparticles from human hair waste followed by the use of these nanoparticles as stabilizers in Pickering emulsion liquid membranes to remove Mn(II) ions is still an untapped area. Hence, the current research focuses on developing a green PELM system using Fe_2O_3 nanoparticles derived from human hair waste and investigating their ability to remove Mn(II) ions under optimal conditions.

There have been numerous research efforts in which the ability of Fe_2O_3 NPs to remediate the environment through degrading and removing pollutants has been demonstrated. In one study, Fe_2O_3 nanoparticles exhibited a high rate of catalytic activity in the breakdown of dyes like methylene blue, where removal efficiencies up to 90% were realized [14]. This is due to the high surface area,

morphology, and strong interfacial interaction abilities of Fe_2O_3 NPs that enable them to be potential candidates for advanced separation processes.

During recent times, considerable research effort has been made into developing environmentally friendly synthesis techniques for the preparation of iron oxide nanoparticles using biological sources like plant extracts or biowastes. Biological approaches provide several benefits, including environmental friendliness, economic feasibility, and low toxicity relative to chemical techniques [15–19]. The technique used for the synthesis is extremely important for defining the shape and physical characteristics of the particles that affect the overall performance of the material in different applications. Specifically, the use of keratinous biowastes like human hair has provided a new sustainable source for nanoparticle production. The efficiency and stability of PELM are largely dependent on various operating conditions, such as the pH of the feed solution, the initial concentration of metal ions, the stirring speed, and the concentration of the stripping agent. The feed solution pH controls the chemical form of the metal ions and the molecular processes at the interfaces. Besides, the concentration of the initial feed solution establishes the concentration difference that propels the diffusion of metal ions through the membrane. Besides, increasing the stirring intensity leads to the formation of smaller droplets and greater contact interfaces, but also enhances the mass transfer rate. However, excessive agitation may lead to the tearing away of the membrane, and therefore the emulsion becomes less stable [20–23].

Taking these developments into consideration, this research is focused on the use of Fe_2O_3 NPs extracted from human hair waste as stabilizers in a Pickering emulsion liquid membrane system to remove Mn(II) ions from water solutions.

MATERIALS AND METHODOLOGY

Materials requirements

Human hair was procured from salons located locally in Chennai, India, to serve as the precursor for synthesis of ferric oxide nanoparticles. Ferric chloride ($FeCl_3$; analytical grade) and sodium hydroxide (NaOH; analytical grade) were bought from Merck Life Science Pvt. Ltd., Mumbai, India. Hydrochloric acid (HCl; analytical grade) was bought from SRL Chemicals, Mumbai, India. Sunflower oil used as the diluent was bought from a local commercial source. Span 80 (sorbitan monooleate), which was used as a surfactant, and tributyl phosphate (TBP), which was used as a carrier, were both obtained from Sigma-Aldrich, USA. Manganese sulphate monohydrate ($MnSO_4$ H_2O), which was used to prepare the feed solution, was bought from Merck, India.

In the emulsion liquid membrane process, each component of the membrane phase contributes to the efficiency of the process in its own way. The first one is the diluent, which consists of sunflower oil and serves as the continuous organic phase in the membrane liquid phase and controls the viscosity and permeability of the membrane [6]. The role of the surfactant Span 80 is to reduce the interfacial tension between the aqueous and organic phases to facilitate the formation and stabilization of emulsion droplets [6,21]. In the case of Pickering emulsion systems, the stability can be further improved due to rigid interfacial layers of Fe_2O_3 nanoparticles that exist in the Pickering system [14,21]. Finally, the role of tributyl phosphate (TBP) as the carrier is that it forms reversible complexes with Mn(II) ions at the interface, which leads to selective transportation of metal ions through the membrane phase and into the internal stripping phase [6,14].

Preparation of Human Hair Extract

The hair was cleaned thoroughly to remove any dirt particles, oils, and surface contaminants that might have become stuck to the hair. The hair was rinsed with distilled water multiple times to ensure that all external contaminants had been removed. The hair was air-dried at room temperature and then cut into smaller pieces to increase surface area to extract the bioactive compounds. Next, a 2 g sample of hair was mixed into 500 mL of deionized water in a borosilicate beaker. The warm water was brought up to 60 °C in a digital heating mantle for 30 minutes (varying heating method). The goal of the heating step was to break down structural proteins, such as keratin, amino acids, and sulfur-containing biomolecules, and extract the compounds into solution. After the heating period had ended, the solution was allowed to cool down to room temperature. Further, it was filtered through Whatman filter paper, and thereby the solid residues were separated. This extract was clear in appearance (light brown) and contained numerous different natural organic compounds. After this process was completed, the hair extract was isolate nanomaterials for various uses planed into a sterile, airtight container to be used later as a reducing and stabilizing agent in the green synthesis of Fe_2O_3 NPs, which were all sourced from the human hair [16–24].

Preparation of Iron Salt Solution

Ferric chloride ($FeCl_3$) solution was made by dissolving 0.1 g of $FeCl_3$ in 500 mL of deionized water. This was the iron source used for nanoparticle synthesis.

Synthesis of Fe_2O_3 NPs

The filtered human hair extract was then gradually added to the $FeCl_3$ solution whilst continuously stirring with a magnetic stirrer at room temperature, to allow for proper dispersion and ensure that the bioactive compounds in the hair extract are not altered. Thirty minutes of stirring continued after the addition of the hair extract before a controlled addition of NaOH; sudden changes of pH in the reaction mixture were avoided, and we ensured a gradual reaction progression. The pH of the mixture was visually monitored until it became close to pH 9-11. This basic environment assisted in the nucleation of Fe and subsequent precipitation of iron oxide (Fe_2O_3) or Fe_2O_3 NPs. The observed reddish-brown precipitate served as a visual confirmation of obtaining Fe_2O_3 nanoparticles. To allow for sufficient growth of Fe_2O_3 particles, the mixed reaction was stirred for a further 30 minutes. Stirring ensured that Ion-oxide nanoparticles (IONPs) were

dispersed well to reduce agglomeration and for complete formation of the iron oxide encapsulated nanoparticles in the bio-assisted green synthesis method [19].

Sonication and Separation

The entire reaction mixture was sonicated using a sonochemical reactor for 30 minutes to further assist with particle uniformity. Following sonication, the mixture was centrifuged at 10,000 rpm for ten minutes. The resulting nanoparticles were collected, ethanol was added to remove residual ions and organic impurities, and they were finally washed twice with double-distilled water.

Drying of Fe_2O_3 NPs

The nanomaterials were oven-dried at 70 °C to obtain a fine powder as shown in Fig. 1. The Fe_2O_3 NPs product was stored in an airtight container for future characterization.

Preparation of feed phase

In a 100 mL beaker, 5 ppm manganese sulphate monohydrate was dissolved in 0.4 M HCl solution. The HCl acts as a Stripping agent. 3ml of Stripping phase is added with the membrane phase to sum up of 10 mL.

Preparation of Membrane Phase

In a 50 mL beaker, the emulsion or membrane phase made of 7 mL as per M/S ratio of 7:3 consists of 14 mL of sunflower oil (diluent) with 2.5 mL of Span80 (surfactant) and tributyl phosphate (Carrier) along with 0.05 g of Fe_2O_3 NPs (Fe_2O_3 Nanoparticles). Then, it is vigorously mixed at 1000 rpm for 10 minutes until an emulsion forms.

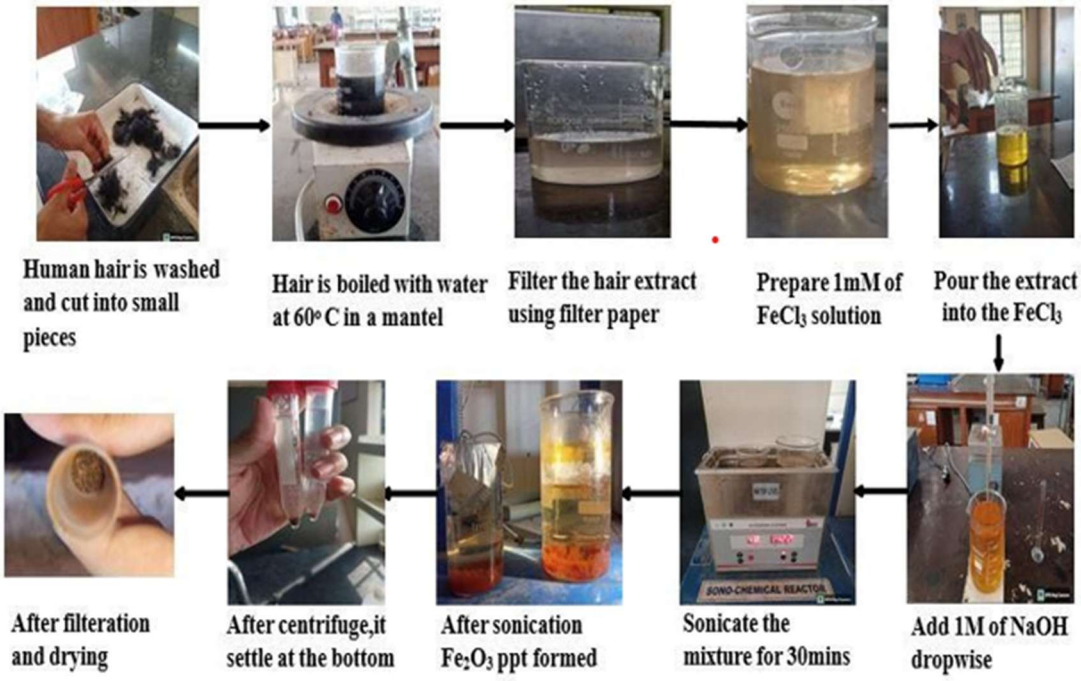


Figure 1. Synthesis of Fe_2O_3 NPs from human hair.

Extraction of Mn(II) Ions

The prepared PELM was added to the feed solution and mechanically stirred at 350 - 400 rpm to form water-in-oil-in-water (W/O/W) double emulsions, ensuring uniform dispersion of the polymeric extract within the solution. The stirring process promoted intimate contact between the phases, facilitating efficient extraction of the target species into the emulsion droplets. After 6 minutes, stirring was stopped to allow the emulsion to stabilize, enabling the dispersed droplets to coalesce and the phases to separate naturally by gravity. The external aqueous phase, which contains the portion of the solute not encapsulated by the emulsion, was carefully collected using a syringe. This phase was then analyzed using atomic absorption spectroscopy (AAS) to accurately determine the concentration of the extracted components, providing insight into the extraction efficiency and performance of the PELM. The extraction of manganese ions is shown in Fig. 2.

ANALYSIS AND CONCLUSIONS

Fourier Transform Infrared Spectroscopy (FTIR) analysis of *Fe_2O_3* NPs

Fig. 3(a) shows the FTIR spectrum of the synthesized Fe_2O_3 NPs in the wavenumber range of 400 to 4000 cm^{-1} to observe the presence of necessary functional groups and the nature of chemical bonding of Fe_2O_3 NPs. The broad absorption band centered at 3222.47 cm^{-1} represents stretching vibrations, which show the presence of hydroxyl groups, most likely from residual NaOH. A peak at 1378.85 cm^{-1} also corresponds to O-H bending vibrations. The band observed at 2351.77 cm^{-1} was attributed to the asymmetric stretching of carbon dioxide (O=C=O). This may have come from exposure to normal air. The peak at 1589.06 cm^{-1}, representing C=C stretching, could be indicative of traces of organic compounds (possible organic functional groups) from hair extract. Importantly, though, the strongest sharp absorbance, below 700 cm^{-1}, was attributed to Fe-O stretching vibrations, indicating the

formation of ferric oxide [16,22,23]. For example, work by Hwang *et al.* [22] distinguished FTIR absorbance bands at 577 cm^{-1} and 631 cm^{-1} corresponding to Fe-O stretching vibrations, clearly showing formed IONPs. Likewise, Niraimathee *et al.* [23] also explicitly stated an absorbance band close to 625 cm^{-1} labelled Fe-O bonds and therefore indicated successful IONPs were made. In addition, a recent paper published in Scientific Reports [24] also presented FTIR peaks attributed to Fe-O stretching vibrations and thus concluded that IONP materials were confirmed with the biological methods. After following through and studying these references, we concluded that the FTIR we obtained shows characteristics *of* Fe_2O_3 NPs [19,23].

X-ray Diffraction Analysis of Fe_2O_3 NPs

X-ray diffraction analysis was employed to characterize the crystalline structure of synthesized Fe_2O_3 NPs; the results are represented in Fig. 3(b). The diffraction peaks seen at 2θ values of 20°–40° exhibited considerable matching with the reflections for iron oxide phases; this showed the nature of crystalline nature, as well as being inconsistent with impurity. Their location corresponds with the JCPDS values for Fe_2O_3 and shows the crystalline structure of these Fe_2O_3 NPs. It shows that there are no other peaks indicating impurities and that no other phase is present. For example, as noted, the XRD patterns for α-Fe_2O_3 nanoparticles (hematite) conform to the JCPDS No. 33-0664, and the XRD peaks for γ-Fe_2O_3 NPs (maghemite) were in accordance with JCPDS Card No. 39-1346. The reference, figures, and evidence provided support the identification and characterization of Fe_2O_3 NPs with X-ray diffraction analysis [11,20].

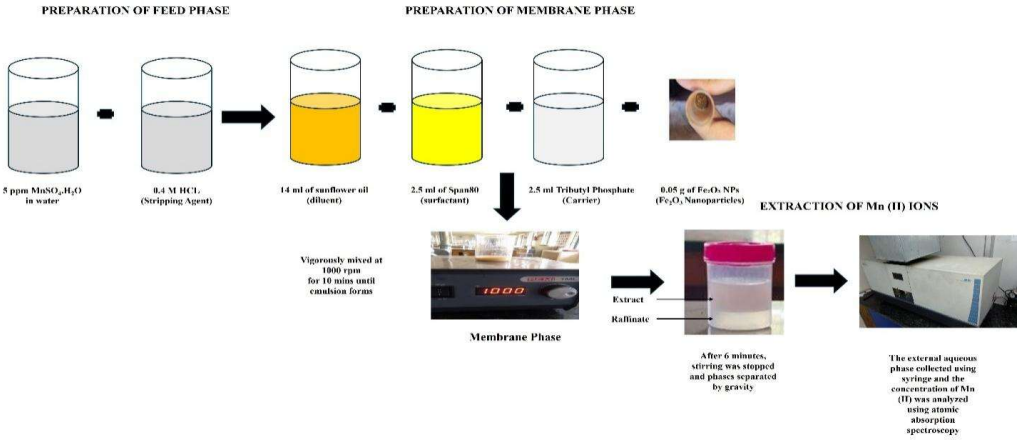


Figure 2. Preparation of PELM and extraction of Mn(II) ions.

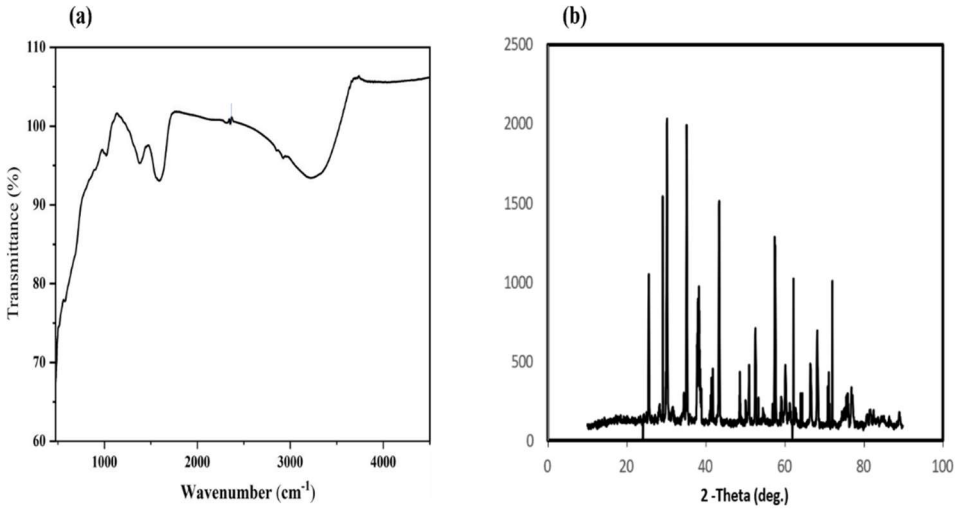


Figure 3 (a) FTIR analysis of Fe_2O_3 NPs; (b) XRD analysis of Fe_2O_3 NPs.

Scanning Electron Microscopy Analysis of Fe_2O_3 NPs

The surface morphology of the synthesized Fe_2O_3 NPs synthesised from Human hair was studied, based on various magnifications (i.e., at 2500 x, 5000 x, 20000 x, and 30000 x, Fig. 4 (a-d)), showing the different shapes and structures of the particles. For initial contrast, the image with the lower magnification, or 2500 x, shows the presence of aggregated, irregularly shaped particles with sharp edges in Fig. 4(a), indicating an incomplete reaction or crystalline cluster when nucleating. In contrast, Fig. 4(b) depicts a compact, rough surface topology with relatively few pores at 5000 x, implying the early stages of particle formation and growth.

As magnification increased, the morphology starts to move towards well-defined flake-like and sheeted structures (i.e., Fig. 4(c), at 20000 x, and Fig. 4(d), at 30000 x), which may have been aided by biomolecules from the

human hair extract that acted as natural stabilizers and capping agents during the particle formation process. The stacks and agglomerates pictured may indicate layered morphologies that could relate to anisotropic growth. In summary, these unique morphologies of the synthesized Fe_2O_3 nanoparticles highlight that there is great diversity in particle shapes, all the way from 500 nm to 10 μm [16,19]. As the particles are irregular in shape and don't appear very spherical in nature, and because they appear to aggregate, it is expected that this may be a reflection of some of the more complex chemical nature of human hair, i.e., cationic keratin proteins, amino acids and some trace metals, that probably manipulate, or act between, the reaction conditions and influence the crystallization conditions and processes during nucleation stage of particle formation. It is also worth mentioning that flaky or platelet-like morphologies of synthesized iron oxides have also been observed in other green syntheses utilizing biowaste or plant-derived precursors. Lastly, their apparent structural characteristics suggest the synthesized Fe_2O_3 nanoparticles will have a high surface area-to-volume ratio of significance for applications related to catalysis, environmental remediation, and antimicrobial modality [13,24].
Moreover, the hierarchical morphology of synthesized particles, relative to the diverse and various scales due to bio-inspired approaches, likely indicates the future potential of innovating biogenic synthesis approaches to control the properties of nanoparticles formed, all while reducing the overall toxic impact on our planetary biosphere [25,26].

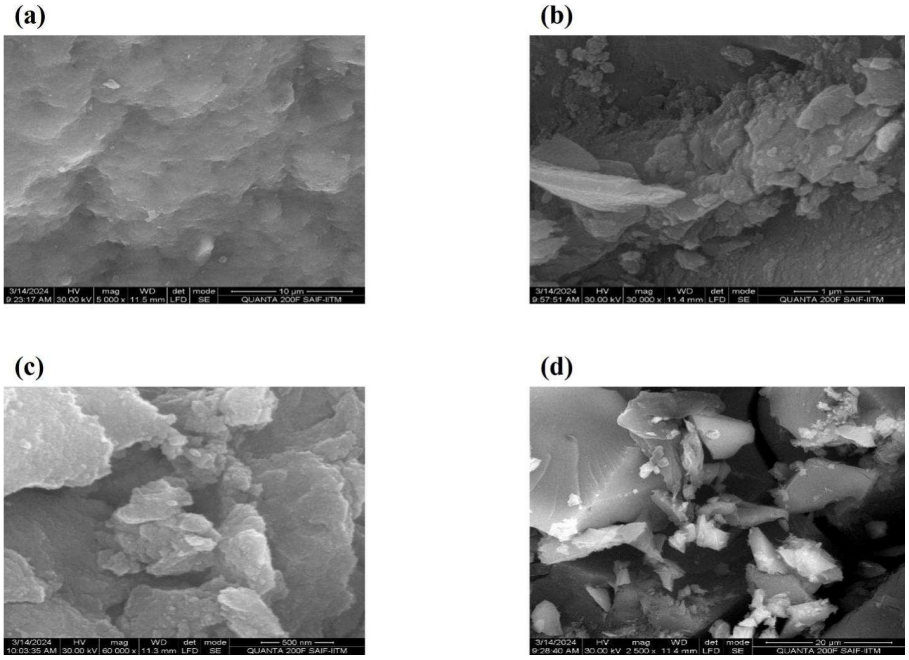


Figure 4 (a) 10 μm, (b) 1 μm, (c) 500 nm and (d) 20 μm SEM images of Fe_2O_3 NPs.

Effect of pH

The effluent was diluted to 5 ppm, and the pH was adjusted from 2.5 to 8.5 with 0.1 N HCl or NaOH to study the effect of changing pH on heavy metal removal. AAS was used as a means to determine the heavy metal removal; in parallel, the corresponding absorbance values are given in Fig. 5 (a). The outcome showed that the extraction efficiency varies inversely with absorbance, where a low level of absorbance corresponds to a high level of extraction efficiency. The absorbance was found to gradually decrease as the pH of the effluent was increased from 2.5 to 8.5 from 2.5, and then suddenly increased afterwards. This shift in behavior is an indication that the extraction efficiency of the PELM system is affected by a change in the effluent pH. A decrease in absorbance indicates an increase in heavy metal removal, whereas an increase in absorbance indicates a decrease in removal efficiency. So, the adjustment of pH with either 0.1 N HCl or NaOH is significant in determining the efficiency of heavy metal removal. The fluctuation in absorbance values observed in this experiment clearly demonstrates that the extraction efficiency is mainly dependent on the pH of the effluent.

Effect of Initial Feed Concentration

The effect of removal efficiency for different levels of initial Mn(II) concentration in the feed solution was observed in a range of 5- 25 ppm with the PELM system under optimized conditions, including an agitation speed of 400 rpm and with feed solution as reported in Fig. 5(b). From the graph, removal efficiency decreased with increased feed concentration. At 5 ppm feed concentration, removal was about 94.31%, while at 10, 15, 20, and 25 ppm feed concentrations, removal decreased gradually to 91.1%, 88.14%, 83%, and 76.10%, respectively. This can be explained by the limited capacity of the carrier and the membrane of the system, which is responsible for transporting Mn(II) ions. There is a concentration difference between the feed and the stripping phase of the carrier. It can be the main reason for Mn(II) movement from the feed across the membrane. Moreover, there is enough membrane and also active sites for transport; that is, the metal ions present in the feed can be accommodated by them. For that reason, the extraction efficiency is relatively high.

The increased feed Mn(II) levels indicate the enormous quantities of Mn(II) to be taken over through the membrane, yet the membrane phase and available transport sites quantity remain practically the same. As a result, metal ions gradually saturate the membrane, and the transport capacity of the PELM system becomes the limiting factor. This leads to a decrease in the removal percentage. In effect, the more metal you have in your feed, the less percent of it you will be able to remove, even if the total transported is higher at higher feed concentration. One reason is that membrane system capacity becomes insufficient to take out an increasingly large fraction of Mn(II) at higher feed concentration. The work showed that the system employing PELM is highly effective for handling solutions that have a low concentration of Mn(II).

Effect of agitation speed

The agitation speed significantly influences the transport of solute across the liquid membrane [27,28]. The impact of agitation speed on the extraction of Mn was investigated over a range of 300–500 rpm, and the results are shown in Fig. 5(c). Agitation speed significantly influences extraction performance by affecting the size and distribution of PELM globules [29,30]. Higher stirring rates produce smaller globules, which increase the interfacial area between the feed and membrane phases, enhancing mass transfer and improving heavy metal extraction. However, speeds beyond the optimum can cause emulsion breakage due to excessive shear forces. During the experiments, as the speed increased from 300 rpm to 450 rpm, extraction efficiency improved from 57.3% to 93.29%. At lower speeds (250–350 rpm), PELM globules did not disperse well, forming larger droplets that reduced extraction efficiency. Maximum extraction (93.1%) was observed at 400 rpm, where emulsion stability was maintained with minimal swelling. Beyond 400 rpm, the emulsion tended to rupture, reducing extraction efficiency due to hydrodynamic instability. A balance between droplet breakage and swelling was observed, and 400 rpm was found to provide optimal membrane stability, enhanced interfacial area, and effective heavy metal removal at 5 ppm aqueous solution in water.

Effect of Stripping Concentration

The influence of the stripping phase concentration (HCl) on heavy metal extraction was evaluated over a range of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 M. The results indicated that 0.4 M HCl provided the highest extraction efficiency, as shown in Fig. 5(d). Increasing the HCl concentration from 0.1 to 0.4 M improved heavy metal removal from 63.8% to 91.1%. However, further increasing the concentration to 0.6–0.8 M led to a decline in extraction efficiency. Higher HCl concentrations increased the emulsion viscosity and reduced the density difference, causing larger droplet sizes and enhanced emulsion leakage due to ionic strength differences between the feed and stripping phases. Consequently, the optimum stripping phase concentration for effective heavy metal extraction was determined to be 0.4 M.

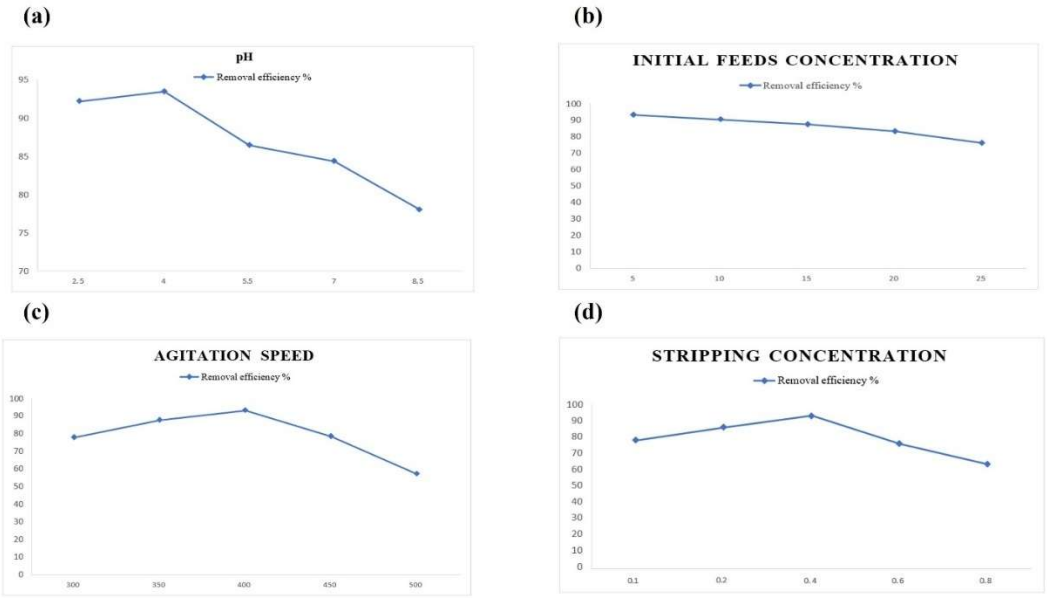


Figure 5 (a) Effect of pH; (b) Effect of initial feed concentration; (c) Effect of agitation speed; and (d) Effect of stripping concentration on Mn(II) ion percentage removal.

CONCLUSION

The current work proved the possibility of obtaining Fe_2O_3 NPs from human hair waste and the use of these nanoparticles as Pickering stabilizers in an emulsion liquid membrane (ELM) for Mn(II) removal. Fe_2O_3 NPs showed typical iron oxide FTIR absorption bands, a polycrystalline structure, and flake-like morphology confirmed by FTIR, XRD, and SEM analysis. The addition of Fe_2O_3 NPs to the PELM resulted in the formation of a stable interfacial film, enabling Mn(II) removal from solution. The influence of different operating conditions, such as the initial pH, Mn(II) content, stirring rate, and stripping agent concentration, was evaluated to optimize the PELM performance for Mn(II) removal. The highest extraction efficiency was achieved at 400 rpm due to increased mass transfer across the membrane. Further increase in the stirring rate led to desta-

bilization of the emulsion. The optimal HCl concentration for Mn(II) extraction was found to be 0.4 M; higher concentrations decreased the extraction efficiency due to membrane damage. The maximum Mn(II) removal of 93.1% was achieved under optimal conditions. The developed method allows for efficient Mn(II) removal while recovering valuable biomaterials from human hair waste. The current work proved the concept of using biowaste as a source of functional nanoparticles for PELM, enabling simultaneous Mn(II) removal and biowaste recycling. However, some aspects require further investigation, including PELM membrane reuse, Mn(II) recovery, and the use of the developed PELM for treating real-world industrial effluents containing target metal ions in trace amounts.

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NAUČNI RAD

UKLANJANJE JONA MANGANA PRIMENOM NANOČESTICA Fe_2O_3 U PIKERINGOVIM EMULZIONIM TEČNIM MEMBRANAMA

Ovo istraživanje usmereno je na ekološki prihvatljivo dobijanje nanočestica oksida gvožđa(III) (Fe_2O_3) iz otpadne ljudske kose, uz istovremeno ispitivanje mogućnosti njihove primene kao Pikeringovih stabilizatora u emulzionim tečnim membranama (PELM) za uklanjanje jona mangana(II) iz kontaminirane vode. Nanočestice Fe_2O_3 sintetisane su sonohemijskim postupkom uz primenu ekstrakta ljudske kose. Karakterizacijom pomoću infracrvene spektroskopije sa Furijeovom transformacijom (FTIR), rendgenske difrakcije (XRD) i mikroskopskih metoda potvrđeno je prisustvo karakterističnih vibracionih modova veza Fe-O, kristalne strukture i morfologije u obliku veoma tankih listića. Ispitana je efikasnost Pikeringovih emulzionih tečnih membrana tipa voda-ulje-voda, zasnovanih na suncokretovom ulju, koje sadrže Span 80, tributil-fosfat (TBP) i hlorovodoničnu kiselinu (HCl), pri različitim vrednostima pH napojnog rastvora, početnim koncentracijama jona Mn(II) (5-25 mg/L), brzinama mešanja (300-500 o/min) i koncentracijama HCl (0,1-0,8 mol/L). Utvrđeno je da efikasnost uklanjanja mangana i stabilnost membrane prvenstveno zavise od brzine mešanja i kiselosti rastvora za reekstrakciju. Pri brzini mešanja od 400 o/min i koncentraciji HCl od 0,4 mol/L postignuta je efikasnost uklanjanja jona Mn(II) od približno 93,1%. Rezultati istraživanja ukazuju na značajan potencijal primene nanočestica Fe_2O_3 dobijenih iz otpadne ljudske kose u procesima uklanjanja teških metala iz vode, kao i na mogućnosti valorizacije biološkog otpada njegovim pretvaranjem u materijale sa dodatom vrednošću.

Ključne reči: otpadna ljudska kosa; nanočestice oksida gvožđa (III); Pikeringove emulzione tečne membrane; uklanjanje mangana; valorizacija otpada.