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Enhancing Removal of Pollutants from Pharmaceutical Wastewater using Ferrites in Membrane Bioreactor

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In recent years, silver-doped ferrites have gained attention as promising materials for the treatment of industrial wastewater in membrane bioreactor (MBR). The current study involved the synthesis of silver-doped nickel ferrite ($AgNiFe_2O_4$) and silver-doped potassium ferrite ($AgKFe_2O_4$) using the sol-gel process, which were specifically designed for the purpose of removing contaminants from the industrial wastewater. The X-ray diffraction (XRD) pattern reveals the single phase cubic spinel structure with space group $Fd\bar{3}m$, while the SEM images demonstrated that an increase in temperature led to a larger sample density and agglomeration of the outer surface of the nanocomposite. Using the membrane bioreactor with $AgNiFe_2O_4$ and $AgKFe_2O_4$ showed dramatically reduction of different contaminants, including microorganisms, in the pharmaceutical wastewater. Furthermore, the regeneration of silver-doped ferrites has been found to be simple and cost-effective, making them an attractive alternative to conventional wastewater treatment methods. Both silver-doped nickel ferrite and potassium ferrite have shown great potentiality for the treatment of pharmaceutical wastewater in MBR technique. However, $AgNiFe_2O_4$ is found to be more effective as compared to silver-doped potassium ferrite ($AgKFe_2O_4$).

Keywords: Silver-doped, Nickel ferrite, Potassium ferrite, Pharmaceutical wastewater, Membrane bioreactor.

INTRODUCTION

Due to its hazardous organic content, pharmaceutical wastewater now poses severe issues for society. Most of them fall under the category of resistant chemicals in hazardous organic pollutants [1]. The disposal of sewage, garbage and pharmaceutical wastes in landfills might result in the persistence of a considerable quantity of biosolids, hence presenting a substantial environmental hazard [2-4]. The presence of organic compounds in drinking water and pharmaceutical wastewater at the micro/nanogram level has been determined using a variety of methodologies [5-11]. When patients take drugs or inject insulin, they generate pharmaceutical waste in their homes [12,13]. Pharmaceutical waste is generated not alone within medical facilities and laboratories, but also within home environments where individuals prescribed medicines and insulin injections [12,13].

In past, several methodologies and strategies were employed for eliminating the potentially harmful or non-biodegradable microorganisms from wastewater. Moreover, conventional wastewater treatment procedures also encounter challenges in eliminating the harmful microbes component from pharmaceutical effluent effectively. It has been observed that the use of Fenton and absorption processes for the purpose of eliminating pharmacologically active substances has been very seldom [14-17]. Current methodologies employed for the total elimination of microorganism contamination frequently involve the utilization of membrane bioreactors. The successful application of membrane bioreactors (MBRs) has been observed in the treatment of pharmaceutical wastewater [18]. In comparison to alternative methods, membrane bioreactors (MBRs) offer expedited initiation of biological processes and enhanced effluent quality [18-24]. In addition to effectively removing nitrogen, phosphorus, turbidity and other contaminants, MBR technology has a smaller impact on the environment, generates less sludge, and has better sludge retention capabilities compared to similar technologies [24-29].

Recently, ferrites played an essential part in facilitating the efficient elimination of metal sludge from wastewater generated by the pharmaceutical industry [30]. Because of their magnetic properties, the catalyst can be easily recovered, and metal sludge can be made [31]. Ferrites, characterized by their enhanced magnetic and electric capabilities are extensively utilized within the wastewater treatment sector. Ferrites were used in greater quantities to remove the hazardous contaminants from wastewater [32]. Several techniques, including sol-gel, ball milling, co-precipitation, hydrothermal and combustion methods, are used to create magnetic nanoferrites [33-37]. Nanoferrites are synthesized using the sol-gel synthesis method, which has proven to be both cost-effective and economical. The magnetic characteristics undergo an alteration when a dopant is introduced. The present study proposes a straightforward approach for synthesizing silver-doped nickel ferrite ($AgNiFe_2O_4$) and silver-doped potassium ferrite ($AgKFe_2O_4$) by the sol-gel process, with the incorporation of silver as an adjuvant to enhance the sensitivity characteristics of ferrites. Both ferrites were characterized and their potentiality towards the removal efficiency of pharmaceutical wastewater were also compared.

EXPERIMENTAL

Sol-gel synthesis: Silver nitrate ($AgNO_3$), nickel ferrite ($NiFe_2O_4$), potassium ferrite (KFe_2O_4), ferric nitrate ($Fe(NO_3)_2\cdot 9H_2O$), citric acid $C_6H_8O_7\cdot H_2O$ were procured from Merck and used as such. Deionized water was used to dissolve the stoichiometric combination of ferrite. In order to obtain a clear solution, the solution was thoroughly combined. Citric acid was added to the ferrite solution to maintain the pH. On a hot plate magnetic stirrer, the prepared solution was being continually stirred. During the heating process, the solution undergoes a phase transition and transforms into a gel-like state. Subsequently, the gel was heated in a oven for 1 h at 250 ºC. The obtained nanopowder underwent a 6 h annealing process at 800 ºC.

Characterization: The X-ray diffraction patterns were obtained using a GBC-Difftech MMA diffractometer and filtered Cu*K*α (λ = 1.54 Å) radiation to investigate the structural characteristics and the incorporation of silver layers on ferrites. The SEM analysis as carried out by using an XL-30 SEM (Philips, Netherlands) instrument.

RESULTS AND DISCUSSION

X-ray diffraction studies: The XRD patterns of silver-doped nickel ferrite ($NiAgFe_2O_4$) and silver-doped potassium ferrite ($KAgFe_2O_4$) are depicted in Fig. 1. A single-phase cubic spinel structure (JCPDS card No. 87-2338) with space group $Fd\bar{3}m$ is evident from the XRD pattern of the produced nanoferrites. The observed peaks 2θ values of the prepared $KAgFe_2O_4$ nanosamples were 30.70º, 36.10º, 44.62º, 54.39º, 57.83º, 63.33º, 77.80º, which correspond to the (220), (311), (321), (421), (333), (440), (620), respectively, while 2θ values of the prepared $NiAgFe_2O_4$ observed peaks 2θ values were 30.72º, 36.12º, 39.01º, 44.66º, 54.43º, 57.99º, 63.67º, 77.90º were indexed to the (220), (311), (222), (321), (421), (333), (440), (620), respectively. Both ferrites are crystalline in nature, when annealed at 800 ºC, both ferrites have well-defined peaks which correspond to other non-stoichiometric metallic ferrites, however, their intensities are low. The crystallite size were calculated by Debye Scherrer equation [38] and $KAgFe_2O_4$ and $NiAgFe_2O_4$ has an average crystallite size of 126 nm and 48 nm, respectively.

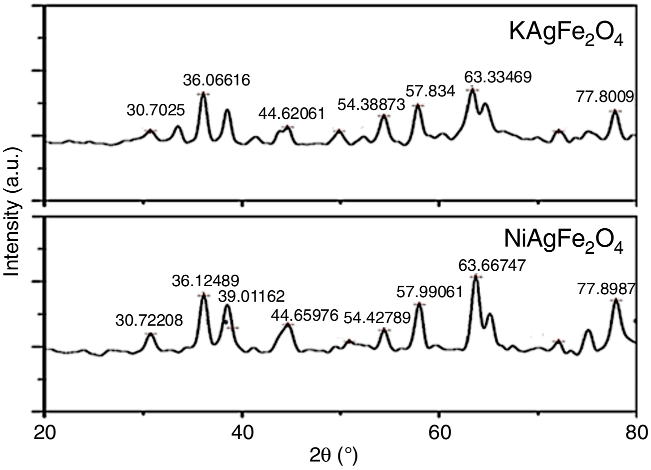

Fig. 1. XRD pattern of $KAgFe_2O_4$ and $NiAgFe_2O_4$ nanoparticles

SEM studies: Fig. 2 shows SEM images, the agglomerated nanoparticles were caused by the magnetic exchange contact between the synthesized ferrites. It is anticipated that the synthesized $NiAgFe_2O_4$ and $KAgFe_2O_4$ ferrities exhibit grain size of 50 nm and 130 nm, respectively. Agglomerated nanoparticles exhibiting the spherical morphology in $NiAgFe_2O_4$ ferrite, owing to their higher surface energy and magnetic interactions. On the other hand, $KAgFe_2O_4$ ferrite displayed with rectangular morphologies.

Application: Membrane bioreactors (MBRs) are a type of wastewater treatment technology that combines biological treatment with membrane filtration to remove pollutants from pharmaceutical wastewater. A thorough comparison of two distinct elements (Ni, K) doped $AgFe_2O_4$ nanoparticles was examined using the raw pharmaceutical wastewater collected from the nearby pharmaceutical industrial area. The physico-chemical characteristic parameters of the collected wastewater sample is shown in Table-1. The initial pH value of the raw water was recorded as 7.57. However, upon $NiAgFe_2O_4$ treatment leads to a decrease in pH, while the introduction of $KAgFe_2O_4$ nanoparticles results in an increase in pH. When the raw water was treated with silver ferrite nanoparticles, the colour of the water was significantly altered. When the ferrite nanoparticles were added to the sample, there were no noticeable changes in the pigment content. The turbidity value was found to be 6.2/NTV for raw water and significantly reduced to less than 1.0 when treated with both ferrites.

The concentration of total suspended solids (TDS) in the untreated wastewater was determined to be 116 mg/L. However, the usage of $NiAgFe_2O_4$ and $KAgFe_2O_4$ nanoparticles resulted in a significant reduction in the concentration of total suspended solids, with values of 14 mg/L and 12 mg/L, respectively. The utilization of ferrite nanoparticles as a remedial measure results in a decrease in the concentration of volatile solids in untreated water, reducing it from 2.38 mg/L to 1.20 mg/L. In terms of total dissolved solids in pharmaceutical wastewater, $NiAgFe_2O_4$ nanoparticles exhibit superior perfor-

TABLE-1
EFFECT OF NANOFERRITES IN REMOVAL OF POLLUTANTS FROM PHARMACEUTICAL WASTEWATER

S. No.	Parameter (s)	Unit	Raw water	Treated by $AgNiFe_2O_4$	Treated by $AgKFe_2O_4$	Permissible limits
1.	pH	–	7.57	7.42	7.58	6.5-8.5
2.	Colour	Hazen	15	5	5	5
3.	Pigment content	mg/L	< 1.0	< 1.0	< 1.0	-
4.	Dye content	mg/L	< 1.0	< 1.0	< 1.0	-
5.	Turbidity	NTU	6.2	< 1.0	< 1.0	1
6.	Total suspended solids	mg/L	116	14	12	-
7.	Total volatile solids	mg/L	2.38	1.20	1.24	-
8.	Total dissolved solids	mg/L	2094	1986	2126	2000
9.	Total organic carbon	mg/L	1.48	1.42	1.42	-
10.	Dissolved oxygen	mg/L	3.6	3.4	3.4	6
11.	Oil and grease	mg/L	2.4	< 1.0	< 1.0	-
12.	Surfactants	mg/L	4.2	3.8	3.8	< 20
13.	Ammoniacal nitrogen as (N)	mg/L	10.72	10.72	10.76	-
14.	Total Kjeldal nitrogen (TKN) as N	mg/L	25.24	25.78	26.42	-
15.	Total alkalinity (as $CaCO_3$)	mg/L	356	306	312	600
16.	Total hardness (as $CaCO_3$)	mg/L	442	424	420	600
17.	Calcium hardness (as $CaCO_3$)	mg/L	284	272	272	
18.	Magnesium hardness (as $CaCO_3$)	mg/L	158	152	148	-
19.	Sodium (as Na)	mg/L	242	242	234	-
20.	Potassium (as K)	mg/L	48	44	76	-
21.	Iron (as Fe)	mg/L	0.16	0.12	0.14	0.3
22.	Phosphate (as PO_4)	mg/L	1.24	1.22	1.16	
23.	Silica (as SiO_2)	mg/L	36.8	32.6	32.4	-
24.	Reactive silica	mg/L	24.4	23.2	22.6	-
25.	Chlorides (as Cl)	mg/L	546	441	427	1000
26.	Sulphate (as SO_4)	mg/L	34	32	32	400
27.	Ammonia (as total ammonia-N)	mg/L	0.76	0.72	0.72	0.5
28.	Free residual chlorine	mg/L	Nil	Nil	Nil	1.0
29.	Suspended particle size	µm	0.2	0.2	0.2	
30.	Bi-carbonate	mg/L	50	46	48	-
31.	Faecal coliforms	MPN/100 mL	-437-	-177-	-185-	Absent
32.	*Escherichia coli*	MPN/100 mL	-115-	-93-	-97-	-
33.	B.O.D (5 days @ 20 °C)	mg/L	124	118	116	
34.	C.O.D	mg/L	372	404	394	-
35.	Algae content	mg/L	24	24	20	-
36.	Bio-mass	mg/L	364	368	372	850
37.	Micro-plastic particles	µm	0.12	0.12	0.12	
38.	Aerobic microbial count	CFU/100 mL	112	Nil	Nil	Absent
a)	Total viable count	CFU/100 mL	154	Nil	Nil	Absent
b)	*Enterobacter*	CFU/100 mL	65	Nil	Nil	Absent
c)	*Pseudomonas*	CFU/100 mL	24	Nil	Nil	Absent
d)	Fungal count	CFU/100 mL	12	Nil	Nil	1.0
39.	Anaerobic bacteria	CFU/100 mL	68	Nil	Nil	Absent
a)	Sulfate reducing bacteria	CFU/100 mL	26	Nil	Nil	Absent
b)	Yeast and mould	CFU/100 mL	18	Nil	Nil	Absent
40.	Total bacterial count	MPN/100 mL	514	Nil	Nil	Absent
41.	Nitrate (as NO_3^-)	mg/L	22	26	22	45
42.	Nitrite (as NO_2^-)	mg/L	14	18	14	
43.	Fluoride (as F^-)	mg/L	0.24	0.22	0.24	
44.	Colloidal particle	µm	1.6	1.2	1.6	
45.	Suspended particle	µm	< 1.0	< 1.0	< 1.0	
46.	Coloidal silica	mg/L	12.4	9.4	9.8	

B.O.D. = Biochemical oxygen demand, C.O.D. = Chemical oxygen demand

mance in comparison to $KAgFe_2O_4$ nanoparticles. The incorporation of $NiAgFe_2O_4$ and $KAgFe_2O_4$ nanoparticles also resulted in a significant decrease in the oil and grease levels within the raw water parameter, reducing them to less than 1.0 mg/L. The similar results are also observed in case of surfactant too.

However, when raw water was treated with $NiAgFe_2O_4$ and $KAgFe_2O_4$ nanoparticles, not much of a change was observed in the total kjeldal nitrogen (TKN) value. Total alkalinity as $CaCO_3$ in mg/L units decreased significantly from 356 mg/L of raw water to 306 mg/L and 312 mg/L. The total

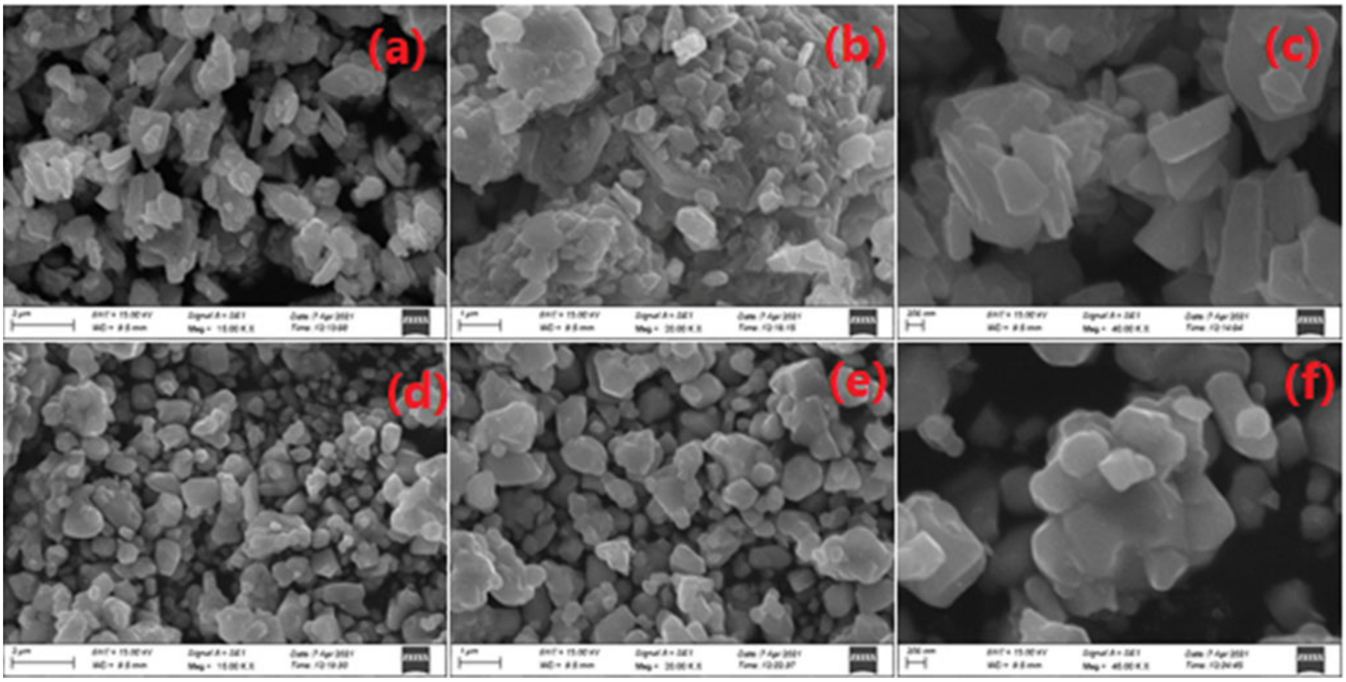

Fig. 2. (a,b,c) SEM images of $KAgFe_2O_4$ and (d,e,f) $NiAgFe_2O_4$ nanoparticles

hardness of the water, as quantified by the concentration of $CaCO_3$, exhibited a decrease for both magnetic ferrites, with values decreasing from 442 mg/L to around 420 mg/L. Compared to raw water, which has a calcium hardness of 284 mg/L, treated pharmaceutical wastewater using $NiAgFe_2O_4$ and $KAgFe_2O_4$ nanoparticles exhibits a calcium hardness of 272 mg/L. $KAgFe_2O_4$ nanoparticle treatment significantly decreased the parameter magnesium hardness value from 158 to 148 mg/L. Potassium was found to be reduced when $NiAgFe_2O_4$ was treated, however, potassium was found to be elevated when $KAgFe_2O_4$ was treated. Furthermore, when the pharmaceutical wastewater was treated with the $NiAgFe_2O_4$ and $KAgFe_2O_4$ particles, additional components including iron, phosphate, silver, chlorides and sulphate were significantly decreased. With the use of spinel ferrites, bioorganic pollutants such as faecal coliforms, *E. coli* and bicarbonate were also significantly decreased.

When silver ferrites are used as a treatment, the BOD (5 days@20 ºC) in the raw water drops to about 118 mg/L. It was shown that nitrate and nitrite values increased when treated with $NiAgFe_2O_4$ nanoparticles and remained as the raw water value under the $KAgFe_2O_4$ nanoparticles. Raw water was found to contain 1.6 m colloidal particles, which were reduced to 1.2 m when treated with $NiAgFe_2O_4$ nanoparticles. Nevertheless, when treated with ferrites, the parameter colloidal silica value decreased to approximately 9.8 mg/L.

Conclusion

A sol-gel method was employed to synthesize $KAgFe_2O_4$ and $NiAgFe_2O_4$ nanoparticles successfully. When analyzed using X-ray diffraction, synthesized nanoferrites have a single phase cubic spinel structure. It demonstrates that the either K and Ni atoms did not alter the interstitial spaces in the $AgFe_2O_4$ matrix when they replaced the silver. The average grain size was found to be 50 nm for $NiAgFe_2O_4$ and 130 nm for $KAgFe_2O_4$ nanoparticles. The removal of hazardous and organic pollutants from the raw pharmaceutical wastewater is often accomplished well by both ferrites in the membrane bioreactor (MBR). A comparative analysis reveals that the total alkalinity reactivity of $AgNiFe_2O_4$ outperforms that of $KNiFe_2O_4$. Overall, these studies suggest that the use of ferrites in MBRs can be an effective method for the removal of pollutants from pharmaceutical wastewater. However, further research is needed to investigate the long-term performance and environmental impact of using ferrites in this application.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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