Comparative Studies on the Chemo and Biosynthesized Nanomaterials for the Remediation of Pharmaceutical Residues in Wastewater

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Received 13 August 2020; accepted 05 September 2020, published online 10 October 2020

Abstract

In the present study, comparison was made on the wastewater remediation efficiencies of chemically and biologically synthesized magnetite and zinc oxide nanoparticles. *Starchytarpheta indica* (snake weed) leaf extract was used as a reducing and capping agent in the green synthesis of magnetite and zinc oxide. The synthesized nanoparticles (NPs) were characterized by X-ray diffraction studies (XRD), Field emission scanning electron microscopy (FESEM) and Fourier transform infra-red spectroscopy (FTIR). These synthesized nanoparticles were further applied in the treatment of industrial pharmaceutical effluent basically comprising amoxicillin, acetaminophen and ascorbic acid. The NPs all performed differently in the removal of these pharmaceutical active compounds. Results showed that the NPs had significant removal efficiencies for acetaminophen, ranging from 67.07 % - 93.59 %, with bio-ZnO having the highest removal efficiency and magnetite giving the least. The range of removal efficiency for ascorbic acid was 54.35 % - 100 %, Magnetite and bio-magnetite showed the highest removal efficiencies whereas bio-ZnO had the least removal rate. Wastewater treatment for the removal of amoxicillin residues with the synthesized nanoparticles was not quite significant, negative removal patterns were observed for wastewater treatment with bio-ZnO and magnetite, a removal rate of 16.82 % was obtained for treatment with bio-magnetite, ZnO NPs had the highest removal efficiency of 49.73 %. Generally, ZnO and bio-magnetite NPs displayed better removal capacities than the other NPs, with overall removal rates of 64.71 % and 48.92 % for ZnO and bio-magnetite NPs respectively.

Keywords: Nanoparticles, pharmaceutical residues, remediation, wastewater treatment

Introduction

The continuous discharge of industrial wastewater into the environment has brought about the release of contaminants of concern such as pharmaceutically active compounds (PhACs) in the aquatic environment. There is global concern that the existence of these contaminants in the environment may lead to adverse human and ecological health effects prompted by their high solubility in water [1]. Numerous pharmaceutically active compounds are found in concentrations of parts per billion or trillion in water bodies. This quantity although minute is sufficient to harm the environment and aquatic life. PhACs are also labeled as hormone disrupters, this implies that these contaminants comprises synthetic hormones, (e.g, estrogen or androgen), which when ingested, can meddle with the normal hormonal processes in animals or humans [2]. PhAC have been discovered to cause infertility,

delayed reproductive development, kidney and liver damage in animals. Synthetic estrogen, present in PhACs has been found to cause hormone interruption in fish, bringing about the feminization of male fish [4].

Apart from industrial discharge and wastewater treatment plants, pharmaceutically active compounds also enter the environment through excretion of drugs taken by humans and animals as inactivated conjugated metabolites of the parent compound. They can also accidentally enter the water supply during manufacturing, handling, and storage. Various manufacturing industries seldom treat their effluents before discharging them into waterbodies, and most WWTPs are not equipped to effectively remove pharmaceutical active compounds from wastewater [5], hence the need for effective treatment method that will remove these contaminant at source before being discharged into the environment.

The potentials of nanoadsorbents such as magnetite and zinc oxide can be harnessed for the treatment of industrial effluents, because of their cost effectiveness and high efficiency in the removal of pollutants. Furthermore, their high surface area-to-volume ratio increases their reactivity with environmental contaminants [6]. These nanoparticles can be synthesized either chemically or biologically, and efforts are being made to make them more environmentally friendly, hence the biological synthesis.

In this study, chemical and biological synthesis methods were employed for the preparation of magnetite and zinc oxide nanoparticles. The leaves extracts of *Stachytarpheta indica* (snake weed) was used for the biological synthesis of both metal oxide nanoparticles. The synthesized nanoparticles were characterized using; FESEM, XRD and FTIR. Finally the nanoparticles were applied as potential adsorbents for the treatment of industrial pharmaceutical effluent, and a comparison was made on their removal efficiencies.

Materials and method

Chemicals

All chemicals, standards and reagents were analytical grade and of highest purity. They include: HPLC grade; Acetonitrile, methanol, water, monobasic sodium phosphate, phosphoric acid, sodium hydroxide, edetate disodium dehydrate, monobasic potassium phosphate. Standards which are chemically similar to the target compounds include; amoxicillin RS (USP), acetaminophen RS (USP), and ascorbic acid RS (USP). These were all supplied by Merck (Germany). Others are: Zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (BDH); sodium carbonate Na_2CO_3 (BDH), Ethanol ($\text{C}_2\text{H}_5\text{OH}$) (Sigma-Aldrich), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O} \geq 99\%$), acetic acid, sodium hydroxide, and 25 % ammonia solution were all purchased from BDH Chemicals Limited, Poole, England. *Stachytarpheta indica* leaves (Michael Okpara University of Agriculture, Umudike).

Adsorbents preparation

Chemical synthesis of Zinc Oxide (ZnO) nanoparticles

ZnO NP was prepared by the precipitation method according to Fouad *et al.*, (2011) [7] and

Mohamed *et al.*, (2012) [8], with slight modification.

Biosynthesis of ZnO nanoparticles

The leaves samples were thoroughly washed with clean water and rinsed with distilled water. The leaves were allowed to dry at room temperature and 20 g was taken for synthesis purpose. The weighed leaves were boiled with 100 mL of distilled water for 20 min at 60 °C. The light yellow coloured solution formed was left to cool. After that, the solution was filtered, and used for the biosynthesis. The biosynthesis of ZnO nanoparticle was carried out using the methods described by Sangeetha *et al.* (2011) [9] and Gnanasangeetha and Thambavani (2013) [10].

Preparation of magnetite nanoparticles (M.NPs.)

Chemical precipitation method as described by Khalil (2015) [11] was employed in the synthesis of magnetite nanoparticles.

Biosynthesis of magnetite nanoparticles

S. indica/ Fe_3O_4 -NPs, was synthesized using the following procedure; Firstly, a solution of Fe^{3+} and Fe^{2+} salts in a 2:1 M ratio was added to the snakeweed extract (50 mL) to obtain a yellowish colloidal solution. Then, a freshly prepared 1.0 M solution of NaOH was added drop-wise to the solution under continuous stirring. The pH of the solution was adjusted to 11, and the solution was then stirred for 1 h to allow complete homogenization. The biomagnetite nanoparticles formed was washed severally with deionized water and dried in an oven at 70 °C for 24 h and stored for further use.

Instrumentation

X-ray diffraction (XRD) patterns and crystallography of the synthesized nanoparticles were recorded using a high-resolution Bruker D8 Advance diffractometer of Cu $\text{K}\alpha$ ($\lambda = 1.54050 \text{ \AA}$) radiation. Morphologies of synthesized nanoparticles were studied using Field emission scanning electron microscopy equipped with an energy dispersive X-ray (EDX) detector (FESEM) (ZEISS ultra plus). Infrared spectra and structural arrangement were obtained by using a Fourier transform infrared spectrometer (FTIR) (Perkin-Elmer Spectrum RX1). Concentrations of the pharmaceutical compounds in the effluent were carried out

quantitatively, using a Hitachi HPLC UV-VIS detector with Elite Lachrom software.

Treatment of pharmaceutical wastewater with NPs

The synthesized NPs were further applied to industrial pharmaceutical effluents to test their removal efficiencies of some drug residues. The wastewater samples were gotten from the effluents of the penultimate and final washings and cleaning of the entire production line for the day's production. Effluent Samples collected after each washing phase was pooled together, the pH was measured, and sample was stored at 4 °C. Triplicate analysis of the effluent was done using HPLC/UV to measure the initial concentrations of drug residues in the effluent samples at pH of 5.5, which was the pH of the effluent sample. The synthesized nanoparticles (ZnO, bio-ZnO, magnetite, and bio-magnetite) (1 g) were then separately added to the effluent sample and were agitated in a fixed speed rotator for a minimum of 180 min. at 400rpm. At the end of the contact time, the samples were filtered and analyzed with HPLC. The percentage removal (% R) was determined using:

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \dots \dots \dots (2)$$

Table1 Chromatographic conditions

Conditions	Acetaminophen	Amoxicillin	Ascorbic acid
mode	LC	LC	LC
UV detector wavelength	243 nm	261 nm	245 nm
Stationary phase (column)	3.9 mm x 30 cm; packing L1	4 mm x 30 cm; 3 to 10 nm packing L1	250 x 4.6 x 5
Mobile phase	Methanol and water (1:3)	Methanol and Buffer (1:19)	Buffer
Flow rate	1.5 mL / min	2 mL / min	1.0 mL / min
Injection volume	10 µL	20 µL	5 mL
Run time	2.150	1.723	3.123

Where C_o is the initial concentration ((mg/L)) of drug residue in sample before treatment and C_e is the final concentration after treatment (mg/L).

Preparation of Standards

Standard stock solutions (100 mg/L) of amoxicillin, ascorbic acid and acetaminophen (paracetamol) were separately prepared in methanol and buffer (1:19) for amoxicillin; diluent (edetate disodium dehydrate and monobasic potassium phosphate) for ascorbic acid and methanol and water (1:3) for acetaminophen. Working standards of 0.5 mg/mL of amoxicillin (USP), 0.25 mg/mL ascorbic acid (USP) and 0.01 mg/mL acetaminophen (USP) were prepared by diluting appropriate aliquots of the stock solutions before each analytical run. All the solutions were stored at 4 °C in the dark.

HPLC analysis

Analyses of the three target drug compounds in the effluent were carried out quantitatively, using a Hitachi HPLC UV-VIS detector with Elite Lachrom software. All system parameters in HPLC were optimized in order to achieve high separation efficiency. Analyses of reference standard solutions were first run, to obtain the peak heights, retention time and area, after which the filtered samples which included untreated and treated wastewater samples were injected directly into the analytical column, and individually ran to yield the initial and final concentrations of the drug residues in the effluent, with reference to their retention times, peak heights and area respectively. Table 1 shows the different chromatographic conditions. In HPLC analysis, quantification was performed by comparing the area of chromatogram of spiked deionized water sample to that of wastewater sample at same retention time. Unspiked de-ionized water was used as a blank sample. The concentration of the analyte was calculated from the peak area.

Results and Discussion

Characterization of Nanomaterials

XRD

The XRD patterns of synthesized ZnO NPs (Fig 1) show peaks corresponding to the crystal planes of (100), (002) and (101) of ZnO along with less noise which suggest that the synthesized sample belong to the hexagonal crystal lattice of the ZnO (JCPDS: 65-3411) [12-13]. The peaks observed were sharp, which indicates that compounds of only ZnO are present with minimum noise distortion or impurities. From the XRD data, it was found that the peaks are broad; suggesting that the crystallites have sizes in the nanometer range. The presence of other phases appears negligible as shown by the spectra. For the bio-ZnO (Fig. 2), the presence of ZnO peaks along with other peaks was observed in the spectrum which indicates that the ZnO formed were completely capped by the biomolecules of the leaf extract. The sharp and narrow diffraction peaks indicate that the product is well crystalline in nature. The calculated average crystallite sizes of both powder particles were about 9 nm for ZnO and 3 nm for bio-ZnO.

Fig. 1 XRD pattern of synthesized ZnO nanoparticles.

Fig. 2 XRD pattern of synthesized *S. indica* bio-ZnO nanoparticles.

The XRD patterns of magnetite and biomagnetite (Figs. 3 and 4), show magnetite peaks at 2θ of 30.36, 35.74, 43.52, 53.95, 57.34 and 63.0° representing the corresponding indices of (220), (311), (400), (422), (511), and (440)

respectively [14-15]. These were compatible with the standard data for Fe_3O_4 peaks (JCPDS: 19-0629). The XRD patterns of biomagnetite showed multiple peaks different from those of magnetite. This implies that the magnetite nanoparticles were mainly amorphous and capped by biomolecules extracted from *Starchytarpheta indica*. Hence the capping activity of the biomolecules might have prevented the detection of the iron oxides [16]. Another reason could also be the incomplete magnetic separation during biosynthesis. However, the very sharp and broad diffraction peaks indicate that the product is well crystalline in nature and this could account for the excellent adsorption performance observed for it. The average crystallite size of the prepared magnetite was 6.4 nm and that of bio-magnetite was 0.026 nm.

Fig. 3 XRD pattern of synthesized magnetite nanoparticles.

Fig. 4 XRD pattern of synthesized *S. indica* biomagnetite nanoparticles.

FESEM

Fig. 5 (a and b) show the SEM images of the ZnO nanoparticles at different magnifications which reveals that the ZnO nanoparticles had flake-like, and porous morphology with less aggregation [9]. The FESEM images of the bio-ZnO nanoparticles with different magnifications are shown in Fig. 6 (a&b), which reveals that the bio-ZnO nanoparticles were spherical and globular with higher degree of agglomeration compared to ZnO. These images also indicate

the availability of nano-size pores and cracks on the surface of the nanoparticles.

Fig. 5 (a&b) SEM images of synthesized ZnO nanoparticles at magnifications of 1000KX and 3000KX.

Fig. 6 (a&b) FESEM images of *S.indica* synthesized BioZnO nanoparticles at magnifications of 3000KX and 10000KX.

The SEM images of magnetite as shown in Fig. 7 (a&b), reveals the presence of aggregates with different shapes and lengths, formed by agglomerated and almost spherical nanoparticles. The agglomeration may be due to magnetic dipole interactions between the particles [17]. The FESEM images of the bio-magnetite nanoparticles (Fig. 8 (a and b)) revealed a sheet-like layer that appeared clumped and cracked, which might be due to the thickening properties of the snake weed (*S. Indica*) or the presence of hydroxyl groups from the extract [18]. Besides, the tendency of agglomeration is not surprising as the synthesized biomagnetite-NPs were very minute in size.

Fig. 7 (a&b) FESEM images of synthesized nano magnetite at magnifications of 1000KX and 3000KX.

Fig. 8 (a&b) FESEM images of synthesized nano bio-magnetite at magnifications of 1000KX and 3000KX.

FTIR

Fig. 9a shows the FTIR spectrum of ZnO nanoparticles synthesized using Zinc acetate and sodium carbonate as precursors. The peak at 468 cm^{-1} shows the characteristic absorption of Zn–O bond. The band at 676 cm^{-1} indicates the stretching vibrations of ZnO nanoparticle. The very intense double peaks at 1384 cm^{-1} and 1500 cm^{-1} are attributed to symmetrical and asymmetrical stretchings of the zinc carboxylate groups, and the absorption at 831 cm^{-1} is due to the lattice vibration of CO_3^{2-} [19]. This also verifies that Na_2CO_3 was one of the precursors used in the synthesis of ZnO nanoparticles. The weak double peaks at 2159 and 2026 cm^{-1} correspond to C–H aldehydic stretching vibration. Broadband at around 3500 cm^{-1} is assigned to O–H stretching mode of the hydroxyl group. This result is in good agreement with other works [20-21].

Fig. 9 FTIR spectrum of synthesized ZnO nanoparticles.

The FT-IR spectra of *S.indica* leaf extract is shown in Figure 10a. The absorption bands at wavelengths of 3761 and 3385 cm^{-1} correspond to O–H stretching vibrations of polyols. Peaks at 2919 and 2850 cm^{-1} also represent C–H

aliphatic stretching of polyols. The sharp peak located at 1639 cm^{-1} represents C=C stretching vibrations of aromatic rings. Stretching vibrations present at 1413 and 1381 cm^{-1} are associated with O-H and C-OH vibrations of polyols, respectively. Stretching vibrations located at 663 cm^{-1} is attributed to N-H stretching vibrations of amines. The small peaks observed at 1730 and 1381 cm^{-1} may be attributed to C=O stretching vibrations of carboxylic acid. These bands indicate the abundance of polyols (phenolic acid and flavonoids), terpenoids, and protein compounds in *S.indica* leaf extract, and may have largely contributed to the reduction of zinc salt to its nanoparticles.

FTIR spectra of biosynthesized ZnO NPs (Figure 10b) shows shifts in absorption bands at 3975 cm^{-1} , 3392 cm^{-1} , 2936 and 2171 cm^{-1} , 1634 and 1551 cm^{-1} , 1493 and 1403 cm^{-1} , 836 cm^{-1} and 472 cm^{-1} respectively. As earlier stated, the peaks in the region between 600 and 400 cm^{-1} correspond to Zn-O, while the band at 472 cm^{-1} confirms stretching vibrations of zinc oxide NPs.

Fig. 10a FTIR spectrum of the chloroform extract of *S. Indica*.

Fig. 10b FTIR spectrum of *S. Indica* synthesized ZnO nanoparticles.

In the FTIR spectrum of magnetite NPs (Fig 11), the presence of absorption bands at 449 , 538 and 2352 cm^{-1} corresponds to the magnetite (Fe_3O_4) phase. The bands observed at 684 cm^{-1}

corresponds to the intrinsic stretching vibration (Fettra $\leftrightarrow$ O) of metal-oxygen at tetrahedral site whereas the band at 449 cm^{-1} corresponds to the stretching vibration (Feocta $\leftrightarrow$ O) of metal-oxygen at octahedral site. Another related report showed that the characteristic absorption bands of the Fe-O bond of bulk Fe_3O_4 were in 570 and 375 cm^{-1} [22]. However, in the synthesized magnetite, these two bands shifted to high wavenumbers of about 538 and 449 cm^{-1} respectively. The peaks at 1609 and 3120 cm^{-1} may be attributed to the stretching vibration of the -OH group of adsorbed water on the surface of the magnetite nanoparticles.

Fig. 11 FTIR spectrum of synthesized magnetite nanoparticles.

The FT-IR spectrum of *S.indica* leaves extract (Fig. 10a), indicated the presence of polyphenols and other biomolecules in the *S.indica* leaves extract and these biomolecules may have participated in the formation of magnetite nanoparticles.

The appearance of a new peak at 589 cm^{-1} (Fig.12) shows the typical characteristic absorption of magnetite nanoparticles. The broad bands at 3821 and 3295 cm^{-1} are assigned to O-H (polyphenolic group) stretching, the weak band at 2158 cm^{-1} corresponds to C-H stretching and a band at around 1582 cm^{-1} can be attributed to the C=C ring stretching in polyphenols. The band at 1351 cm^{-1} corresponds to the C-N stretching vibrations while the medium peak at 1065 cm^{-1} may be attributed to the stretching vibration of C-O-C. Several other peaks in the spectral range $800\text{--}1800\text{ cm}^{-1}$ may also be attributed to the polyphenols that were likely present at the surface of iron nanoparticles.

Fig. 12 FTIR spectrum of *S. Indica* synthesized bio-magnetite nanoparticles.

Analysis of pharmaceutical effluent

Analysis of the pharmaceutical effluent revealed the presence of three pharmaceutical residues (amoxicillin, acetaminophen and ascorbic acid) in various concentrations (Table 2). Amoxicillin had the highest concentration (341.71 mg/l), while the least concentration was observed for acetaminophen (2.5998 mg/l).

Table 2 mean concentration values of pharmaceutical residues

Target compounds	Initial effluent pharmaceutical residue average concentration (mg/L)
Amoxicillin	341.71 ±0.001
Acetaminophen	2.60 ±0.000
Ascorbic acid	212.51 ±0.001

Values= Mean of triplicate values ± Standard error of mean

Treatment of pharmaceutical wastewater with the prepared nanoparticles

The adsorption of pharmaceuticals by adsorbents is mostly influenced by their physical/chemical properties [23], hence treatment of the effluent with the synthesized nanoparticles generally showed insignificant removal of amoxicillin, with ZnO and bio-magnetite nanoparticles having removal efficiencies of 49.73 % and 16.72 % respectively. Negative removal efficiencies and increased concentrations of amoxicillin were observed when the effluent was treated with Bio-ZnO and magnetite (Table 3). This observed increase in concentration may have resulted from (i) amoxicillin's specific characteristics and persistence nature, for

instance its water soluble nature and the low K_{ow} value (0.84) prevents amoxicillin from getting adsorbed onto the nano-adsorbents. Another reason could be the deconjugation of conjugated metabolites during the adsorption process [24]. Furthermore, a change in the adsorption behavior of the target compounds to the nanoparticles during treatment processes may influence their ratio in the treated and untreated water. Then finally pH conditions may also affect the kinetic behavior of the compounds. Similarly, Minh *et al.* (2009) [25] reported very high levels of amoxicillin (1300–1660 ng L⁻¹) in the treated effluents of Hong Kong, and Shishir *et al.* (2011) [26] reported the removal efficiencies of antibiotics as varying between –11.2 and 69 %.

Treatment with the bio-adsorbents (bio-ZnO and bio-magnetite) showed better removal of acetaminophen, with removal efficiencies of 93.59 and 92.81 % respectively when compared with ZnO and magnetite, which had removal efficiencies of 87.43 and 65.07 % (Table 3). High removal efficiencies for acetaminophen have continuously been observed by other researchers [27-28]. This is attributable primarily to the high adsorption sites of the nanoparticles, or microbial degradation, where primary treatment occurs for wastewater treatment plants [29]. Therefore the synthesized nanoparticles are observed to be good adsorbents for the elimination of acetaminophen from pharmaceutical effluents.

From Table 3, ascorbic acid presented high removal efficiencies after effluent samples were treated with the synthesized nanoparticles. Highest removal efficiencies (100 %) were observed for magnetite and bio-magnetite, while treatment with bio-ZnO showed relatively lower percentage removal efficiency of 54.35%. Appreciable percentage removal efficiency of 88.52 % was obtained for ZnO nanoparticles, signifying that the nanoparticles can effectively reduce the concentration of ascorbic acid in industrial effluents.

Table 3 Concentrations of pharmaceuticals (mg mL⁻¹) in wastewater sample after treatment with nano-adsorbents

Detected Target Compounds	ZnO C _o (mg/L)	C _e (mg/L)	%R	Bio-ZnO C _o ((mg/L)	C _e (mg/L)	%R
Amoxicillin	341.71	171.78	49.73	341.71	400.35	-17.16
Acetaminophen	2.60	0.33	87.43	2.60	0.17	93.59
Ascorbic acid	212.51	24.40	88.52	212.51	97.02	54.35
Total pharmaceutical compounds	556.82	196.50	64.71	556.82	497.53	10.65

Table 3 Concentrations of pharmaceuticals (mg mL⁻¹) in wastewater sample after treatment with nano-adsorbents (cont'd)

Detected Target Compounds	Mag C _o (mg/L)	C _e (mg/L)	%R	Bio-mag C _o (mg/L)	C _e (mg/L)	%R
Amoxicillin	341.71	396.35	-15.99	341.71	284.22	16.82
Acetaminophen	2.60	0.9081	65.07	2.5998	0.1868	92.81
Ascorbic acid	212.51	N.D	100	212.51	N.D	100
Total pharmaceutical compounds	556.82	397.26	28.66	556.82	284.41	48.92

Percentage removals of the individual and total pharmaceutical residues in the effluent by the nanoparticles are presented in the charts in Figs. 13 and 14. ZnO showed better removal of amoxicillin in comparison with other nanoparticles as seen in Fig. 13. The percentage removal efficiencies for acetaminophen followed the order: bio-ZnO > bio-magnetite > ZnO > magnetite. Ascorbic acid was also well adsorbed by the nanoparticles, with exception of bio-ZnO that showed less than 60 % removal efficiency.

Fig. 13 Percentage removals of the individual pharmaceutical residues in the effluent by the NPs.

Fig. 14 shows the total pharmaceutical residues removed by the nanoparticles. As seen from the figure, ZnO nanoparticles generally had the highest removal efficiency (64.71 %), followed by the bio-magnetite nanoparticles (48.92 %). Total removal of pharmaceutical residues by bio-ZnO and magnetite nanoparticles were not

very significant, as the removal efficiencies were below 30 %.

Fig. 14 Total removal of pharmaceutical residues by in the effluent by the NPs.

Conclusion

Green and chemical synthesis of ZnO and magnetite nanoparticles can be done using their salts as precursors and the leaf extract of *Starchytarpheta indica* for the green synthesis. The synthesized nanoparticles were characterized by XRD, FTIR and FESEM and further applied in the treatment of pharmaceutical effluent, where ZnO and biomagnetite nanoparticles were observed to have shown better removal efficiencies for amoxicillin, than the bio-ZnO and magnetite. For the removal of acetaminophen, the synthesized bio-nanoparticles of ZnO and magnetite displayed better performance in comparison with the chemically synthesized nanoparticles. Magnetite and bio-magnetite nanoparticles had optimum removal effect for ascorbic acid, while ZnO showed higher removal of ascorbic acid than the bio-ZnO. Generally, the synthesized ZnO and bio-magnetite nanoparticles displayed better percentage removal of total target pharmaceutical residues than the other synthesized nanoparticles, with ZnO having the most effect

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