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Preparation, characterization, and antibacterial activity of $CoFe_2O_4$/polyaniline/Ag nanocomposite

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ABSTRACT

A new magnetically responsive three-component nanocomposite consisting of $CoFe_2O_4$, polyaniline (PANI) and nanosilver has been prepared by coating of $CoFe_2O_4$ nanoparticles with PANI and subsequent immobilization of silver nanoparticles onto the surface of the polyaniline shell. The as-prepared $CoFe_2O_4$/PANI/Ag nanocomposite has been characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and vibrating sample magnetometer (VSM). Inlaying the pre-synthesized $CoFe_2O_4$/PANI composite with silver nanoparticles enhances its electrical conductivity as well as its catalytic and antibacterial activities. The $CoFe_2O_4$/PANI/Ag nanocomposite shows good antibacterial activity against some Gram-positive and Gram-negative bacteria. Although the saturation magnetization of the $CoFe_2O_4$ core decreases significantly on coating with PANI and nanosilver shells, the $CoFe_2O_4$/PANI/Ag nanocomposite can be still separated from water solution through magnetic decantation.

1. Introduction

In recent years, developments of conducting polymers incorporated with magnetic nanoparticles have attracted significant attention because of their potential for combining properties that are difficult to attain separately with the individual components [1,2].

Many researchers have been involved in fabricating new composite materials such as conductive polymers with magnetic behavior or magnetic particles containing conductive polymer [3–5]. Such new materials have unique properties and wide range of potential applications [6–9].

The most common method to synthesize core/shell composites possessing both magnetic and conducting properties is coating of a ferromagnetic material with a conducting polymer [10,11]. Among the various heterogeneous conducting polymers, polyaniline (PANI) is one of the most popular electro-conductive polymers due to its high conductivity, environmental stability, inexpensive monomer and rather simple synthesis [12,13]. On the other hand, spinel ferrites of the type MFe_2O_4 (M is a divalent metal cation) are found to be the most versatile technological materials for advancements in electronics, magnetic storage, ferro-fluid technology, and many bio-inspired applications [14,15]. Therefore, spinel ferrites, such as Fe_3O_4 and $CoFe_2O_4$, are the best candidates as cores for fabrication of core/shell nanostructures having both magnetic and conductive properties [16–18].

It is a general observation that in the absence of surface coating, nanoparticles have the tendency to agglomerate due to their large surface area to volume ratio. The polymer coating can prevent the agglomeration and provides stability to ferrite nanoparticles [19].

There are many reports in the literature devoted to the synthesizing of a magnetic and conductive PANI/MFe_2O_4 nanocomposites, having a core–shell structure, by *in situ* polymerization of aniline with MFe_2O_4 nanoparticles [20–24]. In some of these reports the magnetic and conductive properties of the PANI/MFe_2O_4 nanocomposite were widely investigated due to new possible surface, inter-facial, inter-particles, and exchange interactions between the magnetic nano-particles and the conductive polymer matrix [3,25].

Although two-component PANI/MFe_2O_4 composites, such as Fe_3O_4@PANI and $NiFe_2O_4$/PANI, have been extensively studied, the three-component composites consisting of a magnetic core coated with two shells, *i.e.* polyaniline and noble metal nanoparticles have not been widely explored yet. It is expected that a rational combination of the PANI/MFe_2O_4 core/shell particles together with

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other functional materials (noble metals, semiconductor, *etc.*) would result in three-component composites with integrated and stable optical, catalytic, electrical, and magnetic properties [26–30]. These types of nanocomposites exhibited promising applications in many areas [31]. On the basis of the above considerations, one could combine the collective advantages of magnetic ferrite (such as $CoFe_2O_4$), PANI, and Ag nanoparticles to fabricate multifunctional material with core/shell structure, sharing good stability, catalytic activity, antibacterial activity and magnetic separability.

In this article, the synthesis and characterization of a novel magnetically responsive $CoFe_2O_4$/PANI/Ag nanocomposite is reported. For the preparation of this composite, the magnetic core, $CoFe_2O_4$, was first synthesized by a simple combustion method and this core was then coated with polyaniline *via in situ* oxidative polymerization of aniline monomers to obtain $CoFe_2O_4$/PANI composite with core/shell structure. In the last step, Ag NPs, produced by reduction of Ag^+ ions, were effectively assembled onto the positively charged surface of the pre-synthesized $CoFe_2O_4$/PANI composite to obtain the final $CoFe_2O_4$/PANI/Ag nanocomposite. The antibacterial and catalytic activities of the latter composite have been also studied. Interestingly, the central magnetite core shows strong magnetic response to externally applied magnetic field, thus providing a convenient means for separating of the nanocomposite from solution.

2. Experimental

2.1. Materials and methods

All the chemicals were of analytical grade and were used without further purification. Double distilled, deionized water was used as a solvent. Manipulations and reactions were carried out in air without the protection of inert gas. Fourier transform infrared (FT-IR) spectra were obtained using a FT BOMEM MB102 spectrophotometer. X-ray diffraction (XRD) patterns of the synthesized samples were taken with a Philips X-ray diffractometer (model PW1840) over a 2θ range from 10 to 80° using Cu K_α radiation ($\lambda = 1.54056$ A°). The morphology and size of the $CoFe_2O_4$@PANI@Ag particles were determined by transmission electron microscopy (TEM) using a Philips CM10-HT 100 kV microscope. The FESEM images were obtained using a Hitachi Japan S4160 scanning electron microscope. The magnetic properties of the as-prepared composites were studied using vibrating sample magnetometer (VSM) of Meghnatis Daghigh Kavir Company.

2.2. Preparation of $CoFe_2O_4$ nanoparticles

Cobalt ferrite nanopatricles were prepared by combustion method using cobalt(II) and iron(III) nitrates with known amount of glycine, as a fuel, with molar ratio of 1:2:4, respectively [32]. The mixed precursors were concentrated in a porcelain crucible on a hot plate at 300 °C.

After the mixture reaches the point of spontaneous combustion, it began burning, vaporized all the solution instantly with great deal of foams yielding a brown voluminous and fluffy $CoFe_2O_4$ product in the container. The acquired substance, $CoFe_2O_4$, was ground into a fine powder, washed with deionized water and then dried in an oven at 100 °C for 2 h.

2.3. Synthesis of $CoFe_2O_4$/PANI nanocomposite

The PANI–ferrite composite was prepared by precipitating of PANI on the surface of pre-synthesized $CoFe_2O_4$ nanoparticles. In this procedure, 50 ml of freshly prepared reaction mixture (0.1 M aniline, 0.125 M ammonium peroxydisulfate in 0.5 M nitric acid) was added to 1.0 g of cobalt ferrite at room temperature [33]. The mixture was stirred during the polymerization of aniline, which was completed within 1 h. Next day, $CoFe_2O_4$/PANI nanocomposite was separated magnetically, rinsed with 0.5 M nitric acid and with acetone, and finally dried at 60 °C in a vacuum oven for 6 h.

2.4. Synthesis of $CoFe_2O_4$/PANI/Ag nanocomposite

A reduction chemical method was employed for the immobilization of Ag nanoparticles onto the surface of $CoFe_2O_4$/PANI composite to obtain the novel $CoFe_2O_4$/PANI@Ag nanocomposite. In the first step, 1.0 g of $CoFe_2O_4$/PANI composite was dispersed in $AgNO_3$ solution (0156 M). After vigorous stirring of this mixture for 30 min to ensure the adsorption of Ag^+ ions by the composite nanoparticles, sodium hydroxide solution with a fixed quantity of polyvinylpyrrolidone (PVP), as stabilizer polymer, was added. Finally, a solution of glucose ($C_6H_{12}O_6$), as reducing agent, was introduced into the reaction vessel and the whole mixture was heated at 70 °C to accelerate the reduction reaction. After fixed period of reaction, the prepared $CoFe_2O_4$/PANI/Ag nanocomposite was separated magnetically and washed several times with water to remove any excess of protecting agent and alkaline materials. The black solid product was dried at 80 °C in an oven for 5 h.

2.5. Antibacterial tests

Antibacterial susceptibility test was done on the as-fabricated magnetic materials, based on Kirby–Bauer disk diffusion method. In these tests, four concentrations including 5, 10, 20 and 40 mg/ml of $CoFe_2O_4$, $CoFe_2O_4$/PANI and $CoFe_2O_4$/PANI/Ag were prepared in sterile water and dispersed by sonication. Blank disks (6.4 mm diameter) were saturated by adding 40 μl of each of the prepared nanoparticles and then placed on Muller-Hinton agar culture medium (Merck, Germany) inoculated as lawn culture with standard bacterial species. The tested bacteria were of Gram-positive and Gram-negative including *Staphylococcus aureus* (ATCC 6538), *Bacillus subtilis* (ATCC 6633), *Escherichia coli* (ATCC 25922) and *Pseudomonas aeruginosa* (ATCC 9027). A lawn culture with 0.5McFarland turbidity was prepared using sterile cotton swabs on culture medium. The plates were incubated at 37 °C for 24 h and then the inhibition zone around each disk was measured and recorded based on mm. These standard antibiotics and their concentrations were selected based on the CLSI (Clinical and Laboratory Standards Institute) guidelines [34].

3. Results and discussion

The oxidation of freshly distilled aniline monomer in an acidic aqueous solution by an oxidant, such as peroxydisulfate, yields polyaniline [35,36]. When the *in situ* polymerization of aniline monomers, however, is carried out in the presence of cobalt ferrite nanoparticles, a two-component composite, $CoFe_2O_4$/PANI, is readily obtained. The surface of the as-prepared $CoFe_2O_4$/PANI nanocomposite was then coated with silver nanoparticles *via* a facile chemical reduction procedure [37]. In this method, silver nanoparticles were prepared by reducing silver nitrate in PVP aqueous solution. Glucose was used as mild reducing agent and sodium hydroxide to accelerate the reaction. Nitric acid has been employed as a medium for the polymerization process of aniline in the present study because nitrate counter-ions in the PANI coating of $CoFe_2O_4$/PANI have no interaction with the Ag^+ ions during the immobilization of Ag nanoparticles onto the surface of this composite. Other acids, such as hydrochloric and phosphoric acids, cannot be used; since Ag^+ ions will precipitate as silver chloride or silver phosphate to prevent the immobilization process

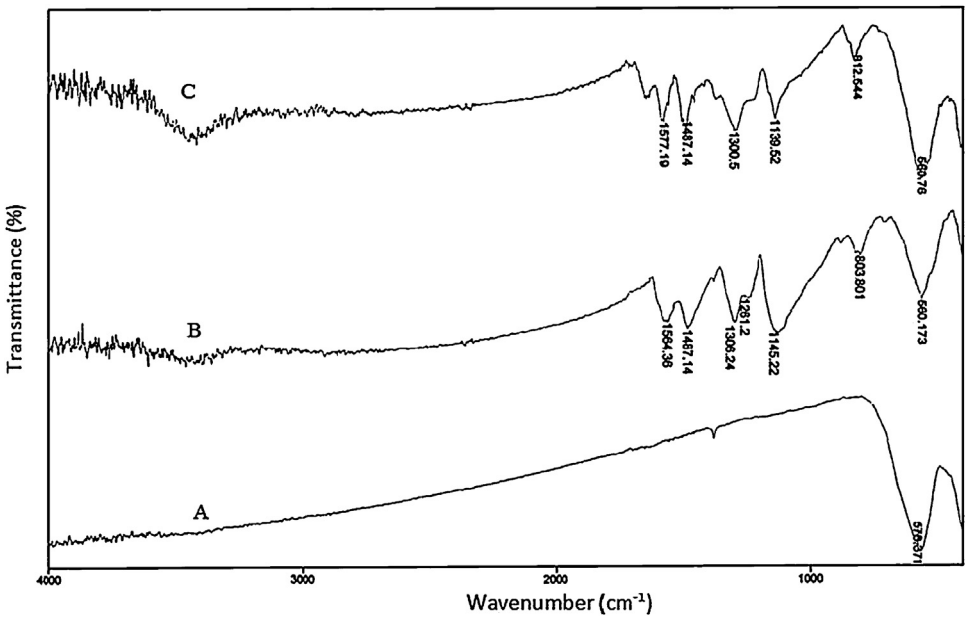
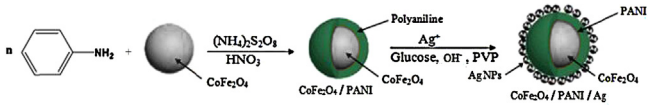


Fig. 1. FT-IR spectra of (A) $CoFe_2O_4$, (B) $CoFe_2O_4$/PANI, and (C) $CoFe_2O_4$/PANI/Ag nanomaterials.

of Ag nanoparticles. The preparation of $CoFe_2O_4$/PANI/Ag nanocomposite is represented in Scheme 1.

The FT-IR spectra of $CoFe_2O_4$, $CoFe_2O_4$/PANI, and $CoFe_2O_4$/PANI/Ag nanoparticles are presented in Fig. 1. In all these spectra two main absorption bands at around 560 cm^{-1} and 420 cm^{-1} are observed. These bands are attributed to the intrinsic stretching vibrations of iron ions in tetrahedral and octahedral sites of the $CoFe_2O_4$ spinel structure, respectively. As it is seen in Fig. 1, the IR spectra of $CoFe_2O_4$/PANI and $CoFe_2O_4$/PANI/Ag nanocomposites, however, exhibit all the characteristic peaks of polyaniline in addition to the Fe–O stretching vibrations. The characteristic peaks of PANI occur at 1564, 1487, 1306, 1145 and 803 cm^{-1}. The peaks at 1564 and 1487 cm^{-1} are attributed to the characteristic C=C stretching of the quinoid and benzenoid rings, the peaks at 1306 cm^{-1} are assigned to C–N stretching of the benzenoid ring, the broad peak at 1145 cm^{-1} is associated with vibration mode of N=Q=N (Q refers to the quinonic-type rings) and the peak at 803 cm^{-1} is attributed to the out-of-plane deformation of C–H in the *p*-disubstituted benzene ring [17,38]. This clearly indicates that the $CoFe_2O_4$ magnetic core was coated with polyaniline and a core/shell nanostructure is formed.

The X-ray diffraction patterns for $CoFe_2O_4$, $CoFe_2O_4$/PANI and $CoFe_2O_4$/PANI/Ag nanomaterials are shown in Fig. 2. The XRD pattern of $CoFe_2O_4$ consists of well-resolved sharp peaks correspond to (*h k l*) planes (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) which mach well with JCPDS (22–1086) file for cubic spinel pure phase of $CoFe_2O_4$. The average crystallite size of the as-prepared $CoFe_2O_4$ nanoparticles was determined by Debye–Scherrer formula and found to be about 30 nm [39]. The same peaks were also observed in the XRD pattern of $CoFe_2O_4$/PANI but with less intensity due to the coating with PANI (see Fig. 2B). The XRD pattern of $CoFe_2O_4$/PANI/Ag nanocomposite, however, reveals four distinct diffraction peaks correspond to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystalline planes of silver with cubic symmetry (JCPDS cards 4–0783), besides to those belonging to $CoFe_2O_4$ nanoparticles. The crystallite sizes of silver nanoparticles were about 30 nm as estimated by Debye–Scherrer formula [40]. This observation confirmed that silver nanoparticles were successfully immobilized on the surface of $CoFe_2O_4$/PANI nanocomposite.



Scheme 1. Step by step preparation of CoFe2O4/PANI/Ag nanocomposite.

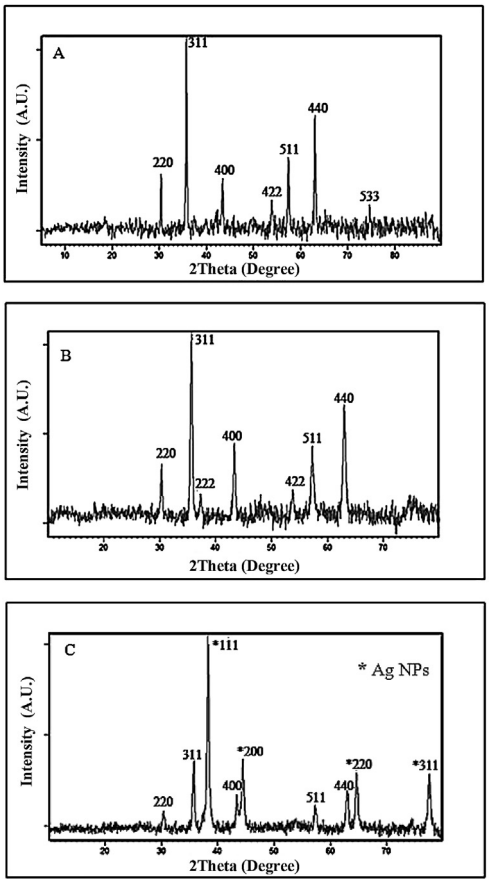


Fig. 2. XRD patterns of as-made (A) $CoFe_2O_4$, (B) $CoFe_2O_4$/PANI, and (C) $CoFe_2O_4$/PANI/Ag.

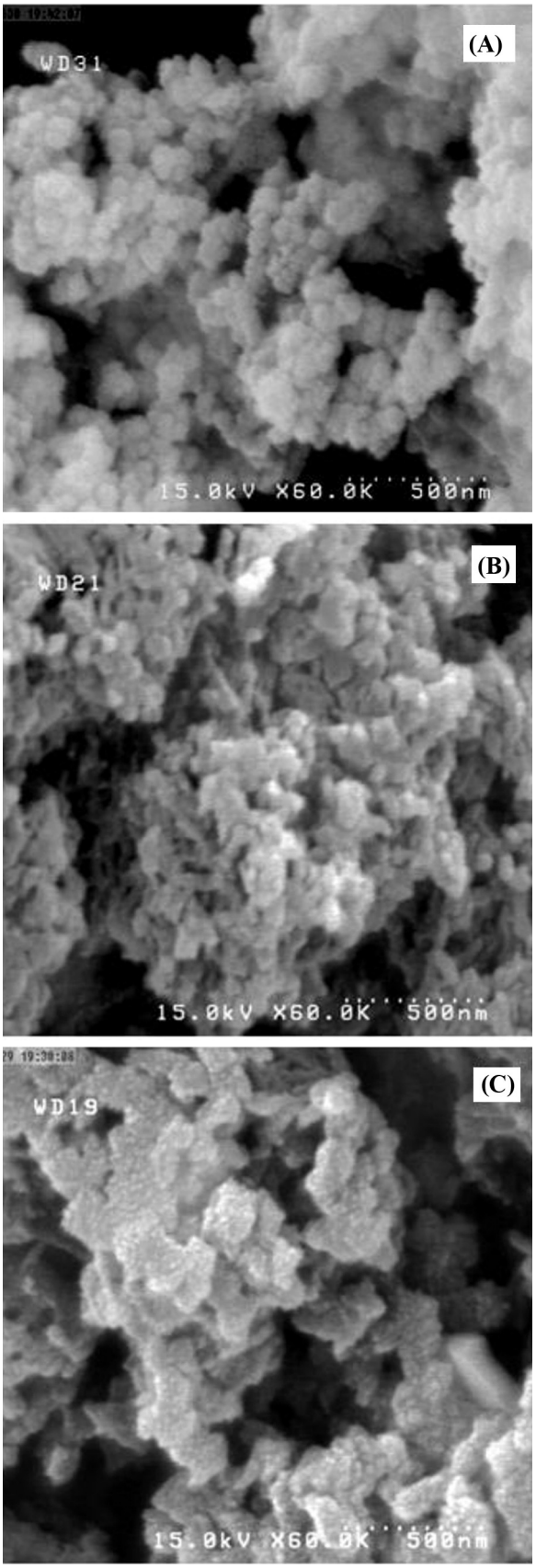


Fig. 3. SEM images of as-prepared (A) $CoFe_2O_4$, (B) $CoFe_2O_4$@PANI and (C) $CoFe_2O_4$@PANI@Ag nanoparticles.

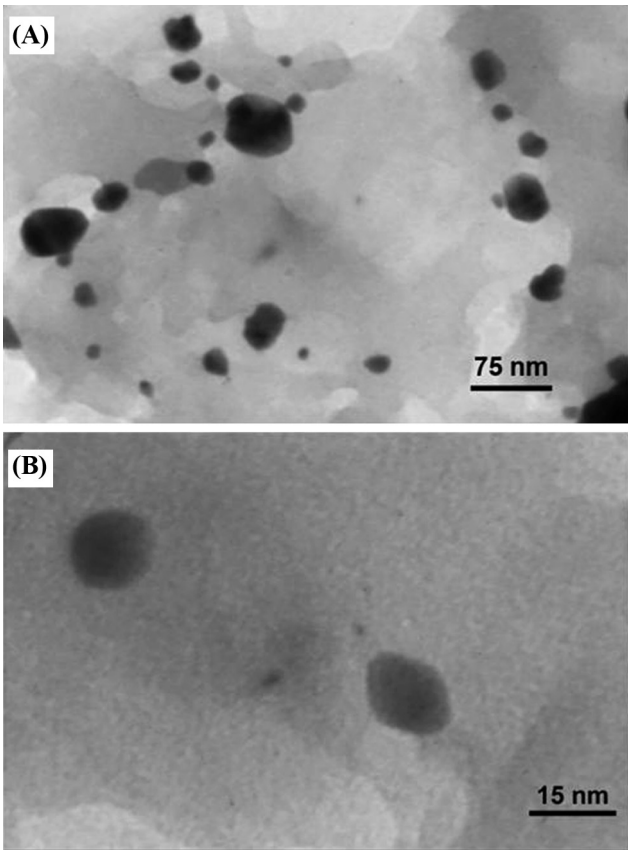


Fig. 4. TEM images of $CoFe_2O_4$/PANI/Ag nanocomposite with two scales.

The morphology of the $CoFe_2O_4$, $CoFe_2O_4$/PANI and $CoFe_2O_4$/PANI/Ag was determined by scanning electron microscopy (SEM). As shown in Fig. 3, the SEM micrographs of these magnetic materials indicate globular agglomerates of irregular microcrystals.

The morphology of $CoFe_2O_4$/PANI/Ag nanocoposite was further explored by high resolution transmission electron microscopy (HRTEM). As it illustrated in the TEM images of this composite (Fig. 4), silver nanoparticles appear as dark nearly spherical spots on the smooth bright surface of the polyaniline coating shell.

The magnetic properties of all the prepared materials were investigated using a vibrating sample magnetometer (VSM) at room temperature and the hysteresis loops are shown in Fig. 5.

The magnetic parameters of $CoFe_2O_4$, $CoFe_2O_4$/PANI and $CoFe_2O_4$/PANI/Ag, including saturation magnetization (M_s), coercivity (H_c) and remnant magnetization (M_r) determined from the hysteresis loops measurements are presented in Table 1. The M_s and M_r values of the nanocomposites are less than those obtained for naked $CoFe_2O_4$ core whereas the H_c value of these composites is higher than that of uncoated $CoFe_2O_4$. The decrease of M_s and M_r values can be attributed to the fact that non-magnetic PANI and silver nanoparticles coating layers on the surface of $CoFe_2O_4$ magnetic particles decreases the magnetism of these magnetic

Table 1
Magnetic parameters of $CoFe_2O_4$, $CoFe_2O_4$/PANI, and $CoFe_2O_4$/PANI/Ag measured by vibrating sample magnetometer.

Compounds	(H_c) O_e	M_r (emu/g)	M_s (emu/g)
$CoFe_2O_4$	848.09	23.45	50.5
$CoFe_2O_4$/PANI	984.06	22.39	44.51
$CoFe_2O_4$/PANI/Ag	871.57	4.07	8.57

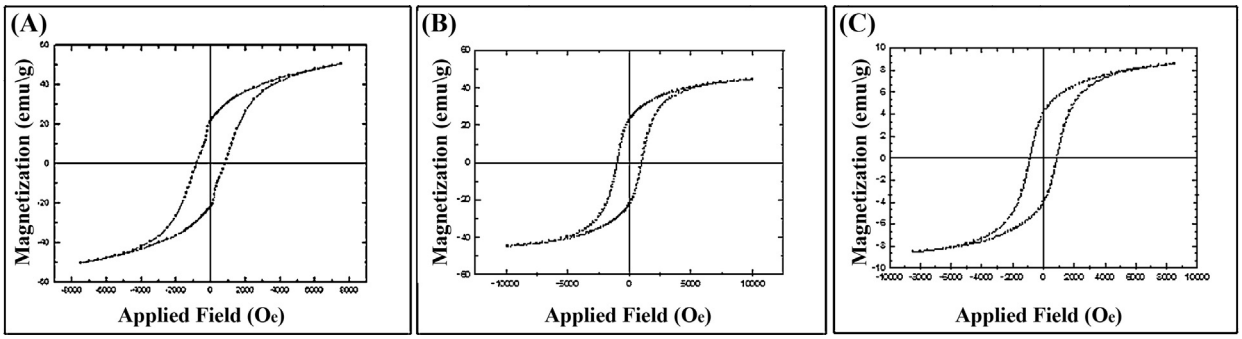


Fig. 5. Magnetization hysteresis loops for: (A) $CoFe_2O_4$, (B) $CoFe_2O_4$/PANI and (C) $CoFe_2O_4$/PANI/Ag.

composites, while the increased coercivity (H_c) value of the nanocomposites can be due to the surface anisotropy upon coating [41,42].

In order to confirm the composition of the as-prepared core–shell $CoFe_2O_4$/PANI/Ag composite particles, EDS analysis was performed in the SEM with a Cu sample holder. The EDS spectrum $CoFe_2O_4$/PANI/Ag, which is shown in Fig. 6, clearly shows the presence of all the main elements (N, O, Fe, Co and Ag) comprising this three-component composite. This finding, in combination with XRD and FT-IR results indicates the presence of $CoFe_2O_4$ particles coated with inner polyaniline and outer Ag NPs layers. The silver content of $CoFe_2O_4$/PANI/Ag nanocomposite was also determined to be 12% (w/w) as documented by the atomic absorption spectroscopy (AAS) analysis. This value is in a close agreement with the silver content of the earlier reported Fe_3O_4–SiO_2–Ag magnetic composite [43] but much higher than the Ag content of Ag@Fe_3O_4 nanocomposite [44].

It is expected that the immobilization of Ag nanoparticles on the surface of $CoFe_2O_4$/PANI affects the conductivity as well as catalytic properties of this nanocomposite. Therefore, electrical conductivity measurement was performed by standard four-point probe method on PANI, $CoFe_2O_4$/PANI and $CoFe_2O_4$/PANI/Ag. Electrical conductivity measurements were carried out with voltage accuracy of 10^{-6} V. As it is seen in Table 2, the conductivity of $CoFe_2O_4$/PANI/Ag nanocomposite is much higher than the conductivities of free PANI and $CoFe_2O_4$/PANI. The enhancement of the PANI conductivity after decorating its surface with silver nanoparticles was also observed by other researchers [45].

Silver nanoparticles have been reported to catalyze various chemical reactions [46,47]. Therefore, it is rather interesting to find out if our newly prepared $CoFe_2O_4$/PANI/Ag nanocomposite can catalyze some chemical reactions. For this purpose, the reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$ in the presence of this composite has been examined. A given amount of the composite was dispersed in aqueous solution containing 4-nitrophenol and then $NaBH_4$ solution was injected under stirring. The reaction was monitored by UV–vis spectroscopy at wavelength range of 240–500 nm. It was noticed that 4-nitrophenol is rapidly and completely converted to 4-aminophenol in the presence of this composite whereas no reaction took place in the absence of the catalyst. The yellow color of the solution vanished, the peak at 395 nm in the 4-nitrophenol spectrum disappeared after reaction, and instead a peak at 298 nm due to 4-aminophenol appeared (see Fig. 7). After the catalytic reaction is completed, the as-prepared $CoFe_2O_4$/PANI/Ag composite catalyst can be efficiently recovered and recycled in the reaction mixtures by magnetic separation.

Although silver has a potent antibacterial activity, the use of Ag nanoparticles as therapeutic agent is limited due to their potential cytotoxic activity against mammalian cells. [47]. Therefore, when silver nanoparticles are used as disinfectant they must be removed from water after disinfection because of their toxicity for the aqua system. The removal of silver nanoparticles from solution media is one of the problems limiting its application. Using the nanocomposite $CoFe_2O_4$/PANI/Ag instead of silver nanoparticles, however, may solve the encountered problem since this composite can be easily separated magnetically from the solution and possible contamination of the disinfectant to the environment is avoided.

The antibacterial activities of $CoFe_2O_4$/PANI/Ag along with other magnetic nanoparticles were studied against some Gram-positive and Gram-negative bacteria and the results of this study,

Table 2
Electrical conductivity values (in S/cm) for the prepared nanoparticles measured by four-point standard method.

Sample	Conductivity (S/cm)
PANI	0.08765
$CoFe_2O_4$/PANI	0.10323
$CoFe_2O_4$/PANI/Ag	0.17491

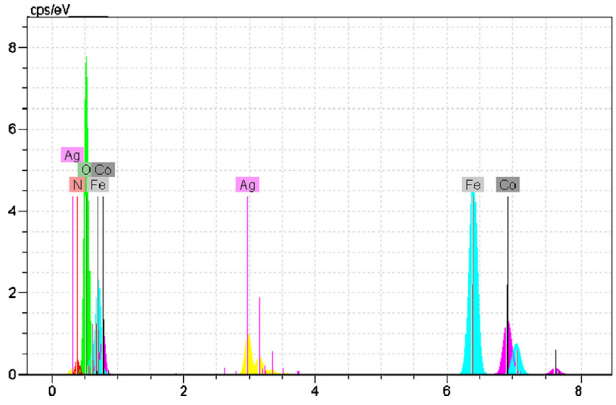


Fig. 6. EDX patterns of $CoFe_2O_4$/PANI/Ag composite.

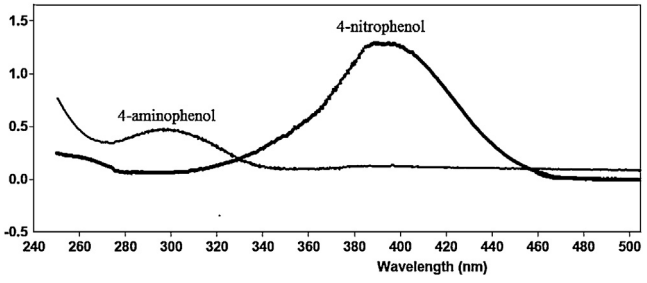


Fig. 7. UV–vis spectra of 4-nitrophenol and 4-aminophenol, obtained by reduction of the former in the presence of $CoFe_2O_4$/PANI/Ag as catalyst. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Mean diameter of inhibition zones (in mm) reflecting magnitude of susceptibility of the microorganism to a certain antibacterial material.

Compounds	Microorganism															
	Gram-positive								Gram-negative							
	S. aureus				*B. subtillis*				*E. coli*				*P. aeruginosa*			
C (mg/ml)	5	10	20	40	5	10	20	40	5	10	20	40	5	10	20	40
$CoFe_2O_4$	–	–	–	–	–	–	–	–	–	–	–	–			–	–
$CoFe_2O_4$/PANI	–	–	–	12	–	–	–	11	–	–	–	7	–	–	–	–
$CoFe_2O_4$/PANI/Ag	13	13	15	17	8	9	10	12	14	14	15	16	7	8	8	11
Nadilixic acid (30 mg)	12	23	25	0												
Cefixime(5 mg)	0	9	18	0												
Penicillin (10 mg)	26	13	12	0												
Streptomycin (10 mg)	12	22	16	0												
Erythromycin(15 mg)	25	27	0	0												
Amoxicillin (25 mg)	28	23	9	0												

i.e. the diameter of inhibition zone (DIZ) in disk diffusion test are presented in Table 3. The DIZ (in mm) is measured by a ruler which reflects the magnitude of susceptibility of the microorganisms to a certain antibacterial material.

As it can be seen from the data of Table 3, the antibacterial activity of $CoFe_2O_4$/PANI/Ag nanocomposite is much higher than $CoFe_2O_4$ and $CoFe_2O_4$/PANI nanopaticles and also higher than some of the tested standard antibacterial drugs. The measured DIZ value for *E. coli* and *S. aureus* bacteria is 16 and 17 mm, respectively (see Table 3). This indicates the potential biocidal effect of the magnetic composite $CoFe_2O_4$/PANI/Ag for different types of bacteria is almost the same. The inhibition zone images of the $CoFe_2O_4$/PANI/Ag nanocomposite against *S. aureus* and *E. coli* for 24 h are also shown in Fig. 8.

Therefore, the as-synthesized $CoFe_2O_4$/PANI/Ag composite can be considered as an antibacterial material with broad spectrum antibacterial ability to both gram-positive and gram-negative bacteria. Our results regarding the antibacterial ability of $CoFe_2O_4$/PANI/Ag nanocomposite are in agreement with other previously reported studies [43,44,48]. In these studies, the antibacterial activities of Fe_3O_4–SiO_2–Ag, Ag@Fe_3O_4 and γ-Fe_2O_3@Ag composites have been investigated by determining the diameter of inhibition zone (DIZ) or minimum inhibition concentration (MIC) of the antibacterial substances. Although the tested materials have shown different antimicrobial activities toward Gram-negative and Gram-positive bacteria, the difference, according to the reported DIZ and MIC values, was not significant. Our finding of the antibacterial activity of the three-component $CoFe_2O_4$/PANI/Ag composite follows the same line obtained by the previous studies. Moreover, immobilization of Ag nanoparticles onto the polyaniline matrix of the composite can exert their antimicrobial activity but their cytotoxic effect on mammalian cells will be expected to be less than free nanosilver because of slow release of silver ions from the matrix.

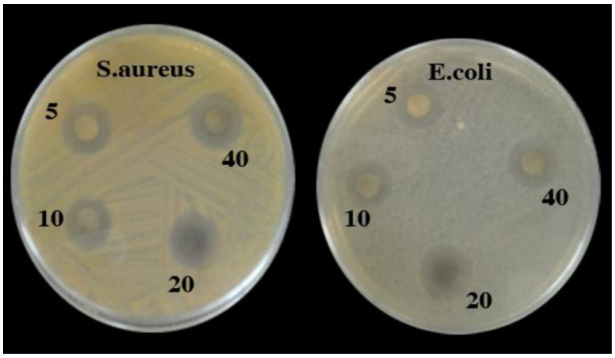


Fig. 8. Photographs of inhibition zone around $CoFe_2O_4$/PANI/Ag composite for *Staphylococcus S. aureus* (left) and *E. coli* (right).

4. Conclusions

The $CoFe_2O_4$/PANI nanocomposite has been prepared by *in situ* polymerization of aniline in the presence of pre-synthesized $CoFe_2O_4$ nanoparticles. The surface of this nanocomposite was then decorated with silver nanoparticles *via* reduction of silver nitrate with glucose in the presence of PVP, as protecting agent, to obtain the new three-component $CoFe_2O_4$/PANI/Ag nanocomposite. The latter nanocomposite was characterized by XRD, FTIR, SEM and HRTEM techniques. The magnetic properties of all the synthesized materials were measured using vibrating sample magnetometer (VSM) at room temperature. The magnetic measurements indicated that the M_s and M_r values of $CoFe_2O_4$ core decrease on coating with polyaniline and silver nanoparticles. The antibacterial activity of the as-made magnetically responsive $CoFe_2O_4$/PANI/Ag nanocomposite was also investigated. The obtained results revealed that this composite has higher antibacterial performance than $CoFe_2O_4$ and $CoFe_2O_4$/PANI nanomaterials and some of the standard antibacterial drugs. This composite was shown to be an efficient catalyst for the reduction of 4-nitrophenol to 4-aminophenol by $NaBH_4$. The composite can be readily isolated from the reaction solution or disinfected media *via* magnetic decantation.

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