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Preparation of magnetic nano-sponge and the effect of its absorption on β-lactam drugs

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The pollution of water with pharmaceutical compounds can cause problems in the ecosystem and their release into the environment may involve long-term risks such as toxicity to aquatic organisms and endocrine disruption in higher organisms. Antibiotics have special importance due to their inducing bacterial resistance. The aim of this study was to optimize the magnetic nano-sponge to adsorption of β-lactam antibiotics.
Magnetic nanoparticles were adopted for the synthesis of magnetic polymeric adsorbents, but the incorporation of magnetic nanoparticles increased the adsorption capacity of polymeric for antibiotics. In this study, we prepared magnetic sponge by lyophilizing the dispersion of $CoFe_2O_4$ nanoparticles and acrylamide for β-lactam adsorption. $CoFe_2O_4$ nanoparticles were attached on MA-PEG, enabling the magnetic property of nano-sponge. The adsorption was moderately fast and could be described by pseudo-second-order model. The as-prepared sponge can selectively absorb β-lactam antibiotic from wastewater.

Keywords: magnetic nano-sponge, β-lactam, antibiotics

INTRODUCTION

In recent years, drug use and the availability of drugs to a variety of people due to the spread of diseases, the progress of medical sciences, pharmacy and therapeutic coverage have increased in the world. Iran is among the top 20 countries in terms of drug use and in Asia after China, it has second place in taking medicine [1].

Pharmaceutical materials in terms of environmental pollution are not the same as other pollutants, such as pesticides and grassland; but in the last decade, with increasing use of medication and, as a result, increasing the production of pharmaceutical substances. The attention of environmentalists has attracted attention [2]. Among antibiotics are the most commonly used drugs [3]. Since the discovery of penicillin, the great developments in antibiotics have been achieved, where pharmaceutical antibiotics has been worldwide used in the treatment of human and animal diseases [4, 5]. However, a huge amount of antibiotics is discharged into the environment during the production, delivery and application [6]. The presence of antibiotics in aquatic environments as emerging contaminant andtheir potential effects on the environment in recent decades have attracted many scientists. Studies have shown that there are different concentrations of antibiotics in sources such as hospital and urban wastewater, wastewater treatment plants, rivers and surface waters, as well as groundwater [7-9]. Pharmaceuticals come in two cycles of water. The first route, which is the industrial method, it includes four stages of production processes, chemical synthesis, fermentation and extraction which often produce high concentrations of wastewater [10]. The second route is through the purchase and use of drugs by people and disposal of antibiotics through urine and stool to sewage (90% of antibiotics are excreted via urine and feces) [11, 12]. About 30-90% of antibiotics does not appear to be metabolized in humans and animals and ultimately enter the environment through active urine and stool [13]. In particular, most antibiotics could not be absorbed and metabolized, thus, antibiotics would be excreted into excreta and released to the environment. The antibiotics pollution leads to several serious hazards [14, 15]. First, antibiotics are toxic to bacteria in water and soil, which would disturb the balance of micro flora and ecosystem. Second, the continuous exposure to antibiotics increases the drug resistance of germs. Third, the uptake of unnecessary antibiotics by human would arouse toxicity in body [16, 17]. Among antibiotics, β-lactam antibiotics used in the treatment of bacterial diseases make up more than 50% of antibiotics [18] and a major part of the chemical drugs [19, 20]. To these regards, it is very important to remediate the antibiotics pollution. β-lactam antibiotics, have been detected in wastewater effluents and their release into the environment may involve long-term risks such as toxicity to aquatic organisms and endocrine disruption in higher organisms. A β-lactam ring is a

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four membered lactam. (Lactam is a cyclic amide, Fig. 1) [21].

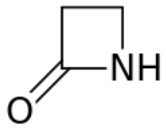

Fig 1. β-lactam ring

One of the main reasons for the treatment of antibiotics is bacterial resistance, which constitute is an important threat to human health [22]. Conventional water and wastewater treatment processes cannot decompose and remove these compounds. So far, various methods have been used such as adsorption of activated carbon, reverse osmosis, air separation and biological methods for the removal of these drug compounds. But these methods do not eliminate pollutants, but only transfer them from one phase to another [23]. Among the efficient treatments of antibiotics, adsorption is widely researched, because adsorption is convenient, fast and economic [24, 25]. Many adsorbents have been applied in the remediation of antibiotics, including active carbon [25], kaolinite [27], palygorskite [28], alumina [26] and chitosan [29]. More recently, nanomaterials show great promising in adsorbing antibiotics due to the large surface area and controllable surface functionalities [30-32]. Among these high-performance nanomaterial adsorbents, Nano-sponges have been regarded as the better effective adsorbent and a good option for removing this antibiotic (β-lactam). The nano-sponge has the ability to absorb material more accurately and better than micrometers. Gel systems have been used in several applications since the middle of the last century. Nowadays, they pervade our world and are very popular in cosmetics, detergents, food, and biomedical applications and in producing numerous products as nanoparticles, dyes, and advanced ceramics using the sol-gel method. Gels can be physical, where the fluid state can usually be recovered by changing the temperature, or chemical, where the gel state is obtained through a polymerization process [33]. Nano-sponges are a new class of colloidal structures based on polymers with large cross-sections. It has nanoscale cavities that can absorb various materials, such as medications [34, 35]. Since these compounds have hydrophobic cavities and hydrophilic outer branches, they can contain hydrophilic and hydrophilic molecules [36-39]. Nano-sponges are small sponges with a size of about one virus with an average diameter of less than 1 μm [40].

The fabricating methods of those reported magnetic sponges are complicated and time-consuming with multiple steps. So it is urgent to develop some one-step facile methods for preparing magnetic sponges with high performance for the adsorption of beta-lactam from wastewater.

Herein, we fabricate a magnetic sponge via one-step facile method throu dipping polyacrylamid for the adsorption of beta-lactam with a high capacity sponge in a suspension containing CoFe2O4 magnetic nanoparticles under ultrasonication was prepared. We report on a new magnetically responsive compartmentalized nanosystem. Functionalized magnetic nanoparticles have been chemically incorporated into a polyacrylamide gel structure to obtain a chemical sponge that can be loaded with microemulsions or micelles solutions and can be used for several different applications (i.e., biotechnology, cosmetics, detergents, etc). The nanomagnetic sponge was obtained by cross linking magnetic nanoparticles through a polymer network based on polyethylene glycol (PEG) and acrylamide. A ferrofluid consisting of positively charged CoFe2O4 nanoparticles in water (0.1 g/mL, 8 nm diameter) was obtained with minor modifications, according to the method developed by Massart.14-17 To cross link the particles, a PEG-based polymer (MA-PEG) was prepared through the esterification of polyethylene glycol with maleic anhydride (MA). The resulting MA-PEG molecules consist of carboxylic groups at both ends of the PEG chain. It has been previously shown that the binding reaction between magnetic nanoparticles and carboxylic acids take the complete coupling of the carboxylic headgroup over the surface of the particles.18 Therefore, MA-PEG was directly reacted with the magnetic nanoparticles, forming a slightly viscous magnetic fluid. Acrylamide and *N*,*N*′- methylene bisacrylamide solutions were then added, and the polymerization reaction was carried out at 50 °C for 4 h, with ammonium persulfate as the radical initiator. Magnetic nanoparticles are embedded in the gel structure via reacting the double bonds of acrylamide or *N*,*N*′-methylene bisacrylamide with the double bond resulting from the esterification of polyethylene glycol with maleic anhydride. (For further information, see Supporting Information.

Magnetic sponge was characterized by scanning electron microscopy (SEM), infrared spectrometer (IR) and magnetometer. The as-prepared sponges show remarkable recyclability and are believed to have wide application in polluted-water treatment.

EXPERIMENTAL SECTION

Materials

$FeNO_3$, $CoNO_3$, Polyethylene glycol (PEG) , Maleic anhydride, Acryl amide, N,N'-Methylene bis acryl amide, NH_3 and Ammonium persulfate were

obtained from Merck Company and used without further purification. The other reagents mentioned are analytical.

Methods

Preparation of positive bonding nanoparticles COFe2O4 (cobalt ferrite). Dissolve 80 g of iron nitrate in 25 ml distilled water. Dissolve 78/3 g of six cobalt nitrate in 25 ml distilled water. Add solutions containing these two mixed salts during stirring with 20 ml of ammonia solution and then PVP with 0.2% v / v. The mixture is poured into a teflon dish with a volume of 125 ml and placed in oven for 3 hours at 190 ° C. A cobalt ferrite is made.

Preparation of magnetic sponges. At first malic anhydride (1 g) and of polyethylene glycol (4 ml) were mixed in a test tube and heat in Ben-Marie at 110 ° C, until the solution begins to boil. Place the test tube at the laboratory temperature to cool (Polyethylene glycol with malic anhydride estrification). Then add the material to the cobalt ferrite. Nanoparticles react with these carboxylic groups, and cobalt ferrite nanoparticles are attached to MA-PEG and a relatively viscous magnetic fluid is produced. 1 g of acrylamide and 1 g of bis-acrylamide and 0.5 g of ammonium persulfate as a radical release and react to 52 ° C for 5 hours.

Characterization of magnetic sponges. The surface morphology of the sample was examined by using a field-emission scanning electron microscope (FESEM, JEOL JSM-7800F, Japan). The composition of the sample was analyzed by X-ray diffractometer (XRD, X'pert PRO, PANalytical B.V., Holland) using Cu Ka radiation (0.15418 nm) and Fourier transform infrared spectrometry (FTIR, Nicolet iN10, USA). The potential interaction between the constituents within the nanocomposite system was analyzed using Fourier transform infrared (FT-IR) spectroscopy at room temperature by a KBr pellet method. The composition of the sample was analyzed by X-ray diffractometer (XRD, X'pert PRO, PANalytical B.V., Holland) using Cu Ka radiation (0.15418 nm).

RESULTS AND DISCUSSION

Nano-sponge characteristics

Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectrum of magnetic sponges is shown in Fig. 2. The β-lactam aromatic rings were reflected by the peak at 1664 (CO) cm^1. Sharp absorption peak 1400 cm^1 are from the characteristic skeleton vibration of the benzene ring, indicating that styrene and 4-tert-butylstyrene have been polymerized into the sponge.

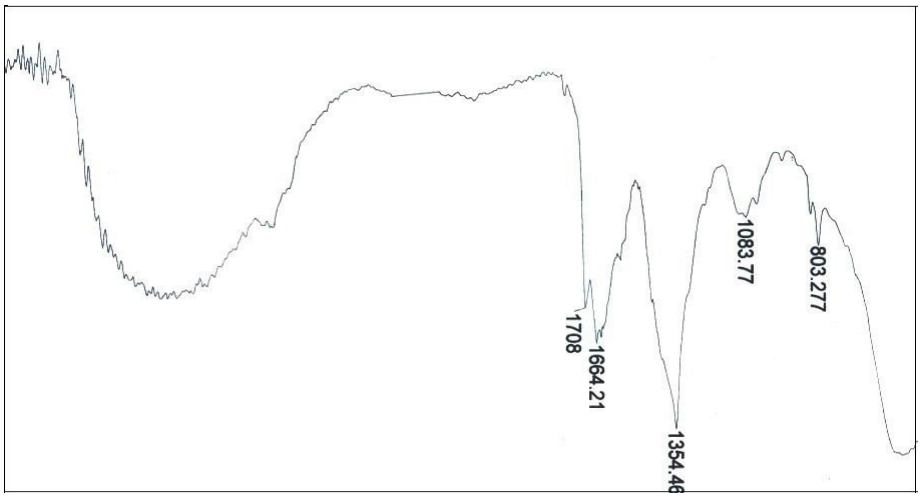

Fig. 2. FT-IR spectrum of a typical magnetic sponge

Morphology observation

The porous structure of magnetic sponge could even be easily recognized by naked eye. The diameters of pores were in the range of 450-629 mm. The SEM characterization collectively indicated that porous structure was formed in nano-sponge and CoFe2O4 nanoparticles were attached on MA-PEG (Figs 3). The attachment of CoFe2O4 nanoparticles was confirmed by the magnetic separation of MA-PEG, too.

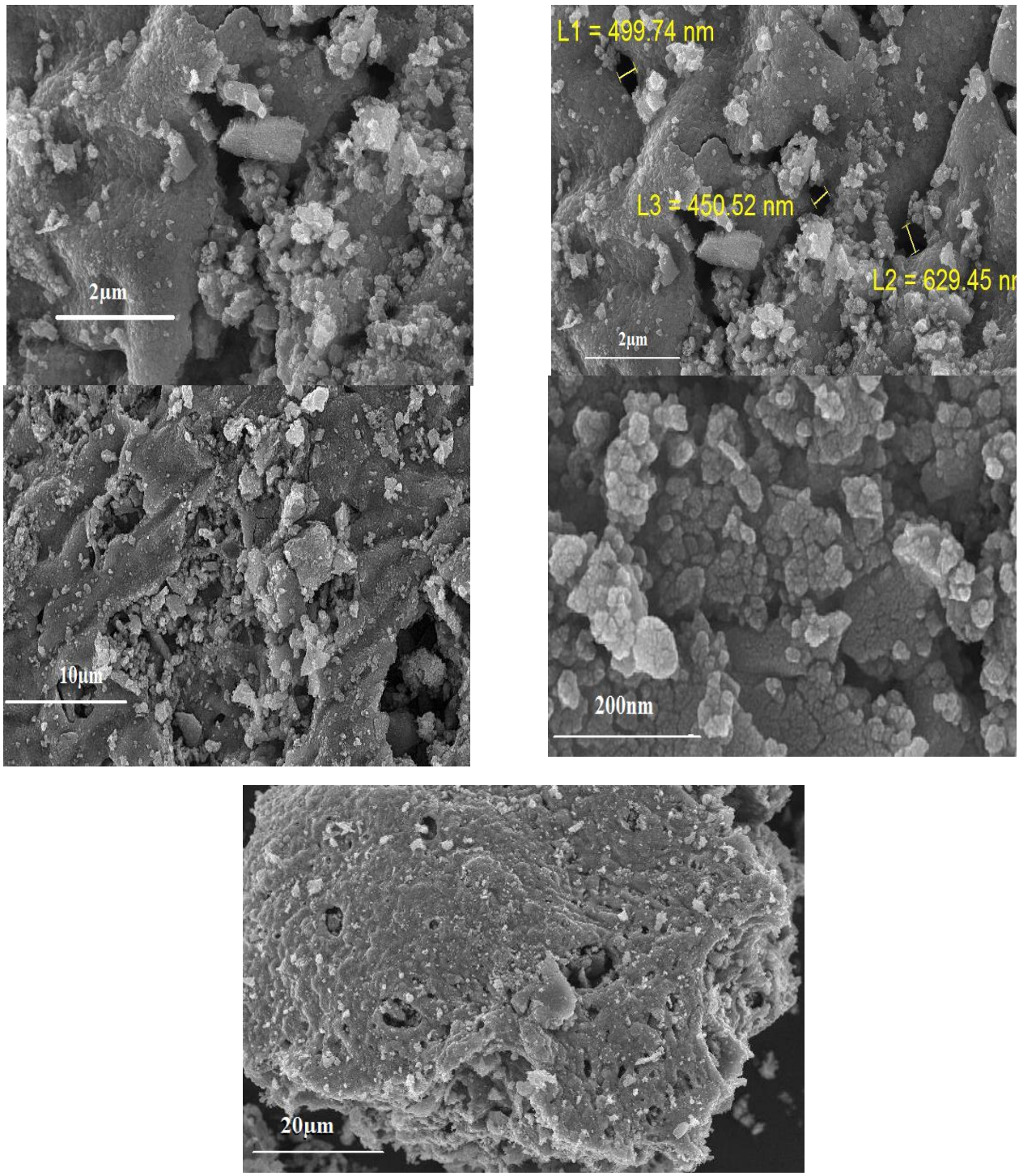

Fig. 3. SEM micrographs.

X-ray diffraction

Characteristic peaks appeared in an XRD pattern of a magnetic sponge (Fig. 4) at 30.1, 35.4, 43.6, 53,5, 57.2 and 62.7, 74, and these peaks correspond to (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) diffraction planes of COFe2O4. The insert is a photo of the absorbent composite, which can be prepared on a large scale because its size can be tailored by the reaction vessels. The sponges are magnetically responsive and can be moved by remote control with a magnet.

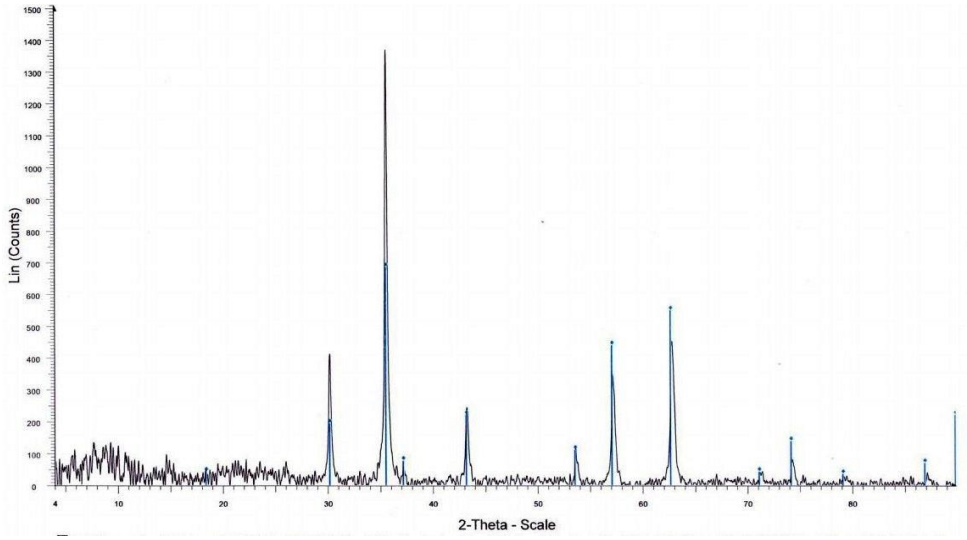

Fig. 4. XRD pattern of a typical magnetic sponge.

CONCLUSION

In summary, a magnetic sponge was facilely fabricated through one-step ultrasonic-assisted dipping treatment in a solution containing compound malic anhydride- polyethylene glycol (MA-PEG) and CoFe2O4 magnetic nanoparticles. The as-prepared sponge can selectively absorb this antibiotic (β-lactam) from wastewater. The as-prepared sponge can be flexibly driven to the polluted water zone by using a magnet. Due to the facile preparation process and excellent performance, such superhydrophobic magnetic sponge will be undoubtedly found wide application in polluted-water treatment and removal antibiotic (betha-lactam) from wastewater.

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