

# Synthesis of Magnetic Nanoparticles under Ambient Temperature from Single Iron Salts and Characterization

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## ABSTRACT

Magnetic nanoparticles (MNPs) have gained a lot of attention from scientists since they offer a great potential in chemistry, biology, medicine, and physics. The synthesis of various types of MNPs for nano-medical products has received a special attentiveness in the recent era. Several methods have been developed for the synthesis of MNPs but most of them need more than one iron precursors, special apparatus, and temperature restriction. In this study, single iron salts and room temperature were considered for the MNPs synthesis which is eco-friendly as well as green methods to reduce the usage of the thermal (heat) energy more Iron salts. An anhydrous Fe (III) salt; ferric chlorides ( $\text{FeCl}_3$ ) were reduced by using potassium iodide (KI) solution. The molar ratio of two salts was 2:1 respectively. The iodine precipitate is filtered out, and the filtrate is hydrolyzed with an ammonium hydroxide solution. Magnetic nanoparticles were synthesized as black precipitated and decanted by external magnet and dried in a desiccator at room temperature. The MNPs were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy energy dispersive X-ray (FESEM-EDX), and vibrating sample magnetometer (VSM). The FTIR spectrum revealed the vibrational stretching band of Fe-O at the peak at  $580 \text{ m cm}^{-1}$ . The crystalline nature of MNPs was determined by XRD analysis. The size of nanoparticles under TEM was  $20 \pm 2.0 \text{ nm}$ . The elemental composition of black magnetite was estimated 51.01 % iron, 38.70% oxygen by EDX. The saturation magnetization of the synthesized nano particles was 66.74 emu/g. This MNPs could be applied in drug delivery systems, protein, enzyme immobilization purposes.

**Keywords:** Anhydrous ferric chlorides; Black precipitated; Magnetic nanoparticles; Magnetization; Potassium iodide

## 1. Introduction

Nanoparticles (NPs) are colloidal solids with sizes ranging from 1 to 100 nanometers. They provide the possibility of interfacing with basic biochemical pathways because their size is fairly similar to those of cells, viruses, proteins, and genetic materials [1]. Nanotechnology is a fascinating new field of study concerned with interactions between particles with sizes from 1 to 100 nm. Nanoproducts have been applied in the domains of health and agriculture, with new applications in healthcare service being developed throughout the world [2]. Nanoparticles (gold nanoparticles) are used to produce hepatitis B virus screening test kits which have higher diagnostic sensitivity, specificity, and accuracy potential [3]. Nanoparticles have also been used as a guideline to enhance the efficacy design of microwave ablation (MWA) and the precious porous liver model is applied for simulation to investigate the improved performance regarding thermal and electrical conductivity [4]. Iron-based nanoparticles are next-generation environmental remediation technology that offer cost-effective solutions to the most difficult environmental cleanup challenges [5]. Through capping compounds, NPs have pharmacological activities such as anti-inflammatory, antifungal, and antiviral activities [6]. While green methods of synthesis have proven beneficial, the use of nanoparticles may be subject to some areas of inherent safety concerns such as biochemical impact on humans and the environment with respect to degradation.

Magnetic nanoparticles (MNPs), by the applying of an external magnetic field and mesoporous materials with a hierarchical pore structure, enhance the rapid and easy separation of the magnetic nano biocatalyst from the reaction volume, ensuring the even dispersal of biomolecules in the matrix pores and thus minimizing enzyme overload and maintaining catalytic action at a higher dimension [7]. MNPs

have got much attention in the biomedical application for their biocompatibility, easy surface modifications and magnetic properties. Magnetic responsive drug carriers consisting of cross-link poly vinyl alcohol (PVA) and magnetic nanoparticles were successfully synthesized [8]. In recent years, much attention has been paid to the synthesis of a different kind of MNPs for nano-medical materials [9]. Khalafalla & Reimers, [10] Massart [11] described first how to make iron oxide magnetic nanoparticles. Following that, a few preparation methods were explored, and such MNPs have shown to have promising magnetic characteristics for a wide range of medical applications [12, 13]. Magnetic nanoparticles are considered materials having great promise in the biomedical field due to their unique features. These include nanometric size, large surface ratio, functioning at the molecular level, excellent magnetic and physicochemical properties, and, most notably, reasonably simple tailoring of all these properties to the particular requirements of various biomedical applications [14].

MNPs have been a subject of discussion in a variety of scientific areas for decades, since they show great promise in a multitude of areas, including chemistry, biology, medicine and physics. Surface characteristics of such nanoparticles are one component that links everything together. Multiple reviews have been published on the surface modification of nanomaterials with polyelectrolytes, with the majority of them focusing on biomedical applications [15-19]. The chemical approaches include a variety of different routes for the preparation of MNPs from the bottom-up synthesis, from which the most renowned ones are discussed shortly. For precipitation, most experimental work uses aqueous media. Ferromagnetic iron oxides are most frequently prepared by co-precipitation from aqueous solutions of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  salts to which a base is added.

Variations in iron salts,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, temperature, pH, and the form of base used can be customized to the magnetic phase and particle size was carried out in ground-breaking work on this preparatory route [10, 11].

The synthesis of various types of MNPs as nano-medical materials has been given a great deal of attention in recent years. Several methods have been developed for the synthesis of MNPs but most of them need more than one iron precursor, special apparatus, and temperature restriction. So, simple, easier, less energy consuming MNPs synthesis methods still need to be established to receive the benefits of its wide applications and usages as a supporting material. The objectives of this investigation were to find out an easy process of magnetic nanoparticles synthesis under ambient condition with no need of thermal application to continue the reaction process. MNPs have been synthesized through a simple co-precipitation technique using anhydrous ferric chlorides ( $\text{FeCl}_3$ ) as a single precursor of iron (III) salts and an additional compound potassium iodide (KI) at room temperature without any external heat energy application.

## 2. Materials and Methods

### 2.1 Chemicals

Anhydrous ferric chlorides ( $\text{FeCl}_3$ ), 25% ammonium solution and potassium iodide (KI) were purchased from R & M, Malaysia and Bendosen, Malaysia. All chemicals were analytical grade.

### 2.2 Synthesis

MNPs were synthesized starting to follow the procedure demonstrated by Khalil [20] with slight adjustment of molar ratio, time, and drying technique.  $\text{FeCl}_3$  and KI had a 2:1 molar ratio. Firstly, 13.168 g of anhydrous  $\text{FeCl}_3$  and 6.584 g of KI powder were fully dissolved individually in 150 ml and 50 ml deionized (DI) water to prepare two aqueous solutions. These two solutions

were then mixed at room temperature (RT), stirred for 30 mins, and allowed to reach equilibrium. The iodine precipitate was filtered out and the filtrate hydrolyzed using 25 ml 25%  $\text{NH}_3$  which was added in dropwise with constant stirring until complete precipitation of the black magnetite was found. The reaction was then left to settle for one hour, black co-precipitant was separated by external magnetic force, and the reaction was washed 5 times with deionized water and dried in a desiccator at RT for 48 hours. The dried black powder was ground in a porcelain mortar and characterized by FTIR, TEM, XRD and VSM for confirmation of iron oxide, size, purity, crystallinity, and magnetization.

### 2.3 Characterization

The FTIR analysis was used to determine that the functional group (Fe-O) exists within the synthesized MNPs. FTIR spectra of dried MNPs samples were conducted using a Perkin Elmer FTIR-ATIR 100 spectrometers in the wavenumber range between 4000 and 400  $\text{cm}^{-1}$ , at a spectral resolution of 4  $\text{cm}^{-1}$ . Around 4-5 mg sample was palletized with 250 mg of potassium bromide (KBr) powder to prepare the pellets. FT-IR analysis was used to determine the specific functional groups that existed within the dried black powder samples through the vibrational stretching.

The dried black powder X-Ray diffraction (XRD) patterns were observed 2 theta range of 10° to 80° utilizing an XRD (Rigaku Mini FLEXII). The phase detection and purity of  $\text{Fe}_3\text{O}_4$  black powder were assessed using XRD data by comparing with Joint Committee on Powder Diffraction Standards (JCPDS) database. The dried black powder samples were examined using TEM (Brand: Fei; Model: Tecnai-G2-20-Twin) at an operating voltage of 200 kV. Before taking the TEM image, the sample was dispersed in ethanol then treated ultrasonically on carbon-coated grids

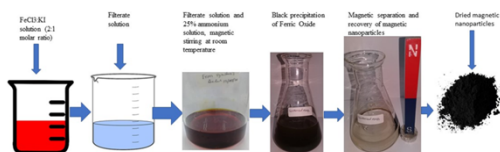
and allowed to dry at RT. Size, shape, and crystal pattern of the synthesized MNPs were evaluated by TEM image at nano level.

The surface properties and morphology of dried black magnetite was visualized and determined with field emission scanning electron microscopy energy dispersive X-ray (FESEM-EDX), (FESEM; Brand JEOL). The magnetic properties of dried black powder samples were examined by vibrating sample. After washing, the black magnetite was kept in a desiccator at room temperature for drying. After completing drying, its weight was 3.142 gram. It carries the complete ferromagnetic behaviors. magnetometer (VSM LakeShore-7407, USA) at room temperature. Magnetic field ( $O_e$ ) was -12,000 to +12,000 and the mass saturation magnetization ( $M_s$ ; emu/g) of the nanoparticles showed on corresponding magnetization curves.

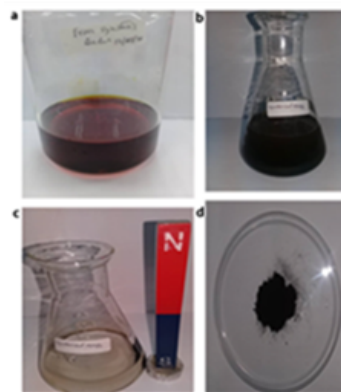
### 3. Results and Discussion

#### 3.1 Synthesis

The co-precipitated black magnetite ( $Fe_3O_4$ ) was produced from reaction mixtures of  $FeCl_3$  salt and KI solution in deionized water. The iodine precipitate was removed by filtration and the filtered solution was hydrolyzed by 25% ammonium hydroxide solution. After keeping the solution for 40 min at RT the black precipitate was found and that was collected by external magnet and washed out five times by deionized water (Fig.1 and Fig. 2).



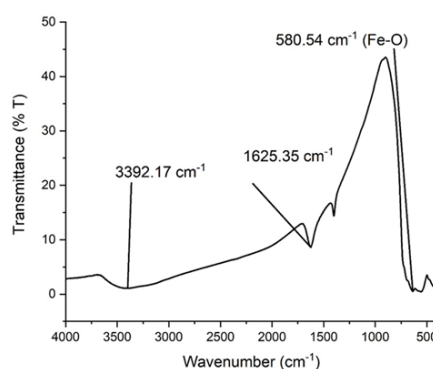
**Fig. 1.** Schematic diagram of magnetic nanoparticles (MNPs) synthesis.



**Fig. 2.** Synthesis, recovery, and dried magnetic nanoparticles (MNPs).

#### 3.2 FT-IR analysis of magnetic nanoparticles

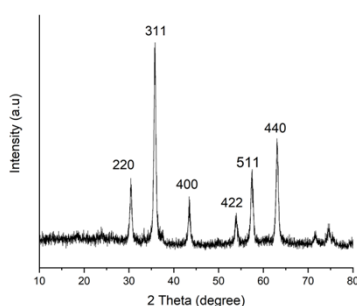
The FTIR spectrum of the dried particles demonstrated bands of vibrations at  $580.54\text{ cm}^{-1}$ ,  $3392.17\text{ cm}^{-1}$  (Fig. 3). The sharp bands at  $580.54\text{ cm}^{-1}$  assigned to the corresponding to the vibration of the F-O bond stretching. From this F-O group existence within the black powders through the FTIR spectrum analysis. The vibrational band at  $3392.17\text{ cm}^{-1}$  proved that the surface of  $Fe_3O_4$  contained hydroxyl groups. It is revealed that the synthesized particles were  $Fe_3O_4$ . This range of bands is evident by other authors [21-24].



**Fig. 3.** FTIR spectrum of synthesized magnetic dried black powder.

### 3.3 XRD Crystal Analysis of Magnetic Nanoparticles

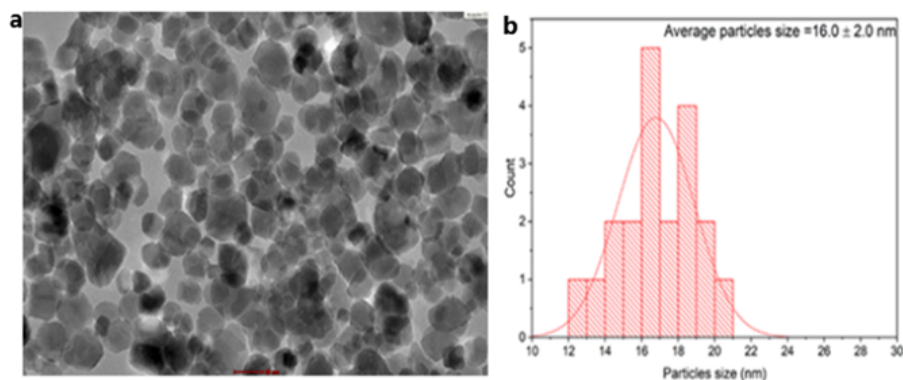
The crystallinity and purity of the synthesized dried magnetic black particles was probed by XRD analysis (Fig. 4). By evaluating the JCPDS code to the XRD graph, the phase and purity of  $\text{Fe}_3\text{O}_4$  black powder were identified. XRD study of dried black powder (Fig. 2) revealed a pattern that was close to the JCPDS code (reference code 01-075-0449). Five characteristics peaks of  $\text{Fe}_3\text{O}_4$  ( $2\theta = 30, 35.5, 43, 53, 57$ , and  $62.6$ ) showed their corresponding intensity indices (220), (311), (400), (422), (511), (440) the sharp diffraction peaks of XRD pattern. The black magnetic particles are a well-defined crystallite, with no phase transition or impurity diffraction peaks, according to the XRD pattern. This result is supported by other researchers [20, 23-24].



**Fig. 4.** XRD pattern of synthesized magnetic dried powder.

### 3.4 Size and morphology analysis of MNPs

Morphology and size of the dried black powder were observed by TEM and shown in Fig. 5. The average diameter of the particles was estimated with ImageJ software [25] and it was  $16.00 \pm 2.00$ . TEM results demonstrated that the dried black powder was completely nano size and shapes of these particles were cubic which is confirmed nano size of the synthesized particles [26]. The surface morphology of the synthesized black magnetite was observed under field emission scanning electron microscope (FESEM) at 200,000 resolutions. Fig. 6a shows that the distribution of the particles is uniform and normal. The elemental composition of black magnetite was estimated 51.01% iron, 38.70% oxygen by EDX. Iron percentage in the black magnetite is shown by the EDX strength peaks (Fig. 6b). This estimation is supported by other researchers [21]. The copper signals came from Cu grid and other signals were not found in the EDX detection limits that verified the  $\text{Fe}_3\text{O}_4$  nanoparticles' purity.



**Fig. 5.** a) TEM image and b) particles size of synthesized magnetic black powder by using Image J software.

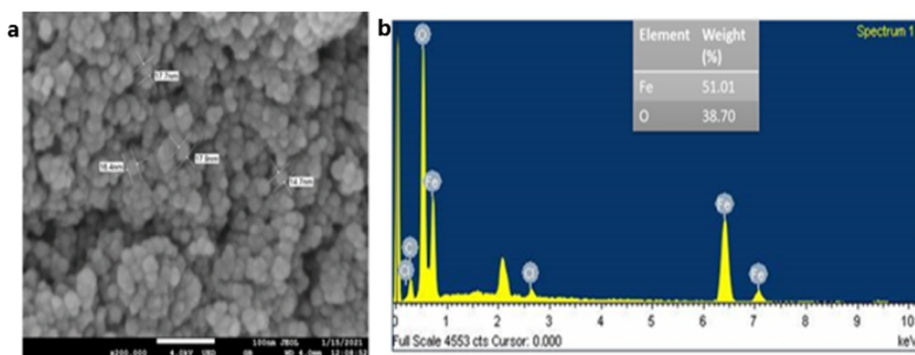


Fig. 6. a) FESEM surface image and b) FESEM-EDX of synthesized MNPs.

### 3.5 Magnetic characteristics of nanoparticles

Magnetic properties of the synthesized dried and grounded nanoparticles were determined by means of vibrating sample magnetometer (VSM). The magnetization ( $M_s$ ) curve of nanoparticles is shown in Fig. 7. The  $M_s$  of the nanoparticle was 66.74 emu/g at 11,782 magnetic field ( $O_e$ ). Owing to the unavailability of magnetic hysteresis it may be deduced that these nanoparticles are superparamagnetic at ambient temperature and have a higher magnetic sensitivity for application in extraction. This finding is supported by other reports [23, 27-28]. So, it is confirmed

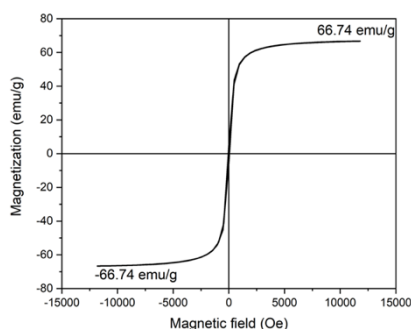


Fig. 7. Magnetization curve of magnetic nanoparticles (MNPs;  $Fe_3O_4$ ).

that the synthesized nano particles are magnetic and showed superparamagnetic behaviors. Magnetic nanoparticles were synthesized from only one ferric chloride salts with noniron salts (KI) at room

temperature and no heat energy is required to the synthesis process. It can be concluded that this magnetic nanoparticle synthesis process is environmentally friendly and easier than any other solvothermal or hydrothermal or solgel methods where heat energy or thermal equipment is essential.

### 4. Conclusion

Magnetic nanoparticles ( $Fe_3O_4$ ) were successfully synthesized at room temperature from single iron (III) ( $FeCl_3$ ) salts by co-precipitation method which is greener and environmentally friendly as well as easier compared to conventional hydrothermal or sol-gel methods. Existing synthesis methods need more thermal and power investment, and special apparatus which leads to environmental pollution. This process has no need of external heat application to the reaction mixture for magnetic nanoparticles synthesis. The synthesized nanoparticles were magnetic and almost homogenous in size. Instead of mixing two precursors of  $Fe(III)$  and  $Fe(II)$ , in a 3:1 mol ratio to synthesize black magnetite, it can be started with just an aqueous iron (III) salts and reduce it with potassium iodide to keep the mole ratio 2:1. Optimization study is further needed to find out better process condition and achieve the higher amount MNPs. These MNPs could be applied in drug delivery systems, protein, enzyme immobilization purposes. Iron based magnetic nanoparticles may be next-

generation environmental remediation technology that will solve the most important environmental challenges.

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### References

- [1] McNamara K, Tofail SAM. Nanosystems: the use of nanoalloys, metallic, bimetallic, and magnetic nanoparticles in biomedical applications. *Phys. Chem. Chem. Phys.* 2015;17(42):27981-95.
- [2] Owaid MN, Naeem GA, Muslim RF, Oleiwi RS. Synthesis, characterization and antitumor efficacy of silver nanoparticle from agaricus bisporus pileus, basidiomycota. *Walailak J. Sci. Technol.* 2020;17(2):75-87.
- [3] Augkarawaritsawong S, Srisurapanon S, Wachiralurpan S, Areekit S, Chansiri K. Comparatively rapid screening tests for diagnosis of hepatitis b virus infection using loop-mediated isothermal amplification (LAMP) paired with lateral flow dipstick (LFD), gold nanoparticles (AuNPs) and real-time turbidimetry. *Sci. Technol. Asia* 2019;24(2):45-57.
- [4] Pongpakpien S, Shaichompu N, Rattanadecho P. Targeted therapy in liver tumor: Study on nanoparticle assisted with porous liver model. *Sci. Technol. Asia* 2021;26(2):87-98.
- [5] Vijaya BRA, Yusop Z, Jaafar J, Veera MRY, Aris A, Abdul MZ, Talib J, Madhavi G. Recent progress on Fe-based nanoparticles: Synthesis, properties, characterization and environmental applications. *Journal of Environmental Chemical Engineering* 2016;4(3):3537-53.
- [6] Yong DWY, Lieu ZZ, Cao X, Yong XE, Wong JZL, Cheong YS, Browder LK, Chin WS. Biogenic Synthesis of Silver Nanoparticles with High Antimicrobial and Catalytic Activities using Sheng Di Huang (Rehmannia glutinosa). *Chem Asian J.* 2021;16(3):237-46.
- [7] Zdarta J, Meyer AS, Jesionowski T, Pinelo M. A general overview of support materials for enzyme immobilization: Characteristics, Properties, Practical Utility. *Catalysts* 8(2), 2018.
- [8] Li J, Gopalan AI, Lee KP. Synthesis of magnetic nanoparticles incorporated smart gel. *J. Nanosci. Nanotechnol.* 2015;15(9):7202-10.
- [9] Biehl P, Von der Lüh M, Dutz S, Schacher FH. Synthesis, Characterization, and Applications of Magnetic Nanoparticles Featuring Polyzwitterionic Coatings. *Polymers* 10(1), 2018.
- [10] Khalafalla S, Reimers G, Preparation of dilution-stable aqueous magnetic fluids. *IEEE Trans. Magn.* 1980;16(2):178-83.
- [11] Massart R. Preparation of Aqueous Ferrofluids without Using Surfactant-Behavior as a Function of the pH and the Counterions. *Comptes Rendus Hebd. des Seances l Acad. des Sci. Ser. C*, 1980;291(1):1-3.
- [12] Krishnan KM. Biomedical nanomagnetics: a spin through possibilities in imaging, diagnostics, and therapy. *IEEE Trans. Magn.* 2010;46(7):2523-58.
- [13] Pankhurst QA, Thanh NTK, Jones SK, Dobson J. Progress in applications of magnetic nanoparticles in biomedicine. *J. Phys. D. Appl. Phys.* 2009;42(22):p. 224001.
- [14] Monteserín M, Larumbe S, Martínez AV, Burgui S, Francisco Martín L.



- Recent Advances in the Development of Magnetic Nanoparticles for Biomedical Applications. *J. Nanosci. Nanotechnol.* 2021;21(5):2705-41.
- [15] Ansari SAMK, Ficiarà E, Ruffinatti FA, Stura I, Argenziano M, Abollino O, Cavalli R, Guiot C, D'Agata F. Magnetic Iron Oxide Nanoparticles: Synthesis, Characterization and Functionalization for Biomedical Applications in the Central Nervous System. *Materials* (Basel). 2019;12(3):465.
- [16] Wu W, Wu Z, Yu T, Jiang C, Kim WS. Recent progress on magnetic iron oxide nanoparticles: synthesis, surface functional strategies and biomedical applications. *Sci. Technol. Adv. Mater* 2015;16(2):023501.
- [17] Xing R, Liu G, Zhu J, Hou Y, Chen X. Functional magnetic nanoparticles for non-viral gene delivery and MR imaging. *Pharm. Res.* 2014;31(6):1377-89.
- [18] Cao B, Tang Q, Cheng G. Recent advances of zwitterionic carboxybetaine materials and their derivatives. *J. Biomater. Sci. Polym. Ed.* 2014;25(14-15):1502-13.
- [19] Veisheh O, Gunn JW, Zhang M. Design and fabrication of magnetic nanoparticles for targeted drug delivery and imaging. *Adv. Drug Deliv. Rev.* 2010;62(3):284-304.
- [20] Khalil MI. Co-precipitation in aqueous solution synthesis of magnetite nanoparticles using iron(III) salts as precursors. *Arab. J. Chem.* 2015;8(2): 279-84.
- [21] Chen X, He B, Feng M, Zhao D, Sun J. Immobilized laccase on magnetic nanoparticles for enhanced lignin model compounds degradation. *Chinese J. Chem. Eng.* 2020;28(8):2152-9.
- [22] Qiu X, Wang Y, Xue Y, Li W, Hu Y. Laccase immobilized on magnetic nanoparticles modified by amino-functionalized ionic liquid via dialdehyde starch for phenolic compounds biodegradation. *Chem. Eng. J.* 2020;391 (Sep. 2019).
- [23] Shanmugam S, Krishnaswamy S, Chandrababu R, Veerabagu U, Pugazhendhi A, Mathimani T. Optimal immobilization of *Trichoderma asperellum* laccase on polymer coated Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles for enhanced biohydrogen production from delignified lignocellulosic biomass. *Fuel* 2020;273:117777.
- [24] Liu X, Chen X, Li Y, Wang X, Peng X, Zhu W. Preparation of superparamagnetic Fe<sub>3</sub>O<sub>4</sub>@ alginate/chitosan nanospheres for *Candida rugosa* lipase immobilization and utilization of layer-by-layer assembly to enhance the stability of immobilized lipase. *ACS Appl. Mater. Interfaces* 2012;4(10):5169-78.
- [25] Gan PG, Sam ST, Abdullah MF, Firdaus Omar M, Tan LS. Alkaline deep eutectic treatment. *BioResources* 2020;15(1):1154-70.
- [26] Mogharabi-Manzari M, Heydari M, Sadeghian-Abadi S, Yousefi-Mokri M, Faramarzi MA. Enzymatic dimerization of phenylacetylene by laccase immobilized on magnetic nanoparticles via click chemistry. *Biocatal. Biotransformation* 2019;37(6):455-65.
- [27] Abbaszadeh M, Hejazi P. Metal affinity immobilization of cellulase on Fe<sub>3</sub>O<sub>4</sub> nanoparticles with copper as ligand for biocatalytic applications. *Food Chem.*, 2019.
- [28] Zhang Q, Kang J, Yang B, Zhao L, Hou Z, Tang B. Immobilized cellulase on Fe<sub>3</sub>O<sub>4</sub> nanoparticles as a magnetically recoverable biocatalyst for the decomposition of corncob. *Cuihua Xuebao/Chinese J. Catal.* 2016;37(3):389-97.