

Effect of iron chlorine concentration on type of green synthesized iron oxides nanoparticles using *Phoenix dactylifera* L leaves extract

A. Labbi^{a,b}, B. Benhaoua^{a,c}, K. Ahmouda^b, Y. Meftah^{a,b}, Kh. Benhaoua^{b,c,*}

^aLab. VTRS, Faculty of Technology, Univ. El-Oued, El oued 39000, Algeria

^bFaculty of Exact Sciences, Univ. El-Oued, El oued 39000, Algeria

^cUnité de Développement des Energies Renouvelables dans les Zones Arides, El oued 39000, Algeria

Iron oxide nanoparticles (NPs) were prepared by green synthesis process, using *Phoenix Dactylifera* L. leaves ethanolic extract as polyphenols source and FeCl_3 aqueous solution as precursor, where the volume ratio was 1:2. The concentration of FeCl_3 was varied as follows: (0.01, 0.02, 0.03 and 0.04M). To characterize the obtained iron oxide NPs, XRD, SEM, UV-VIS and FTIR techniques were used. XRD analyses show the existence of three essential compounds of iron oxide NPs: maghemite phase, hematite phase and beta phase. While the grain size of these compounds was varied in the ranges of 22.91-37.40nm, 20.41-31.32nm and 17.96-25.25nm respectively. SEM images analysis showed that all samples have spherical shaped particles. UV-VIS analysis showed that the variation of FeCl_3 concentration has a direct effect on the band gap of the product which ranged in the range 2.162-2.358eV, whereas FTIR study confirms the abundance of Fe-O bonds in all samples.

(Received July 1, 2021; Accepted December 15, 2021)

Keywords: Iron oxides nanoparticles, Maghemite Fe_2O_3 , Hematite Fe_2O_3 , beta- Fe_2O_3 , Green synthesis, *Phoenix dactylifera* L.

1. Introduction

In general NPs have an enhanced magnetic, optical, electronic, catalytic and biological properties that differ from those in the massive materials, due to their size and shape characteristics. In the last years, NPs have taken a lot of interest because of their use in different applications due to their distinguishable properties which offer them a higher intrinsic reactivity via their surface sites area [1]. Particularly iron oxides NPs are widely used in specific fields applications, such as biomedical field: treatment of hyperthermia for cancer cells [2, 3], in molecular biology [4, 5] (DNA and cell purification, protection of human cells from ultraviolet rays), in earth science [6]. In industry, NPs are also used to develop magnetic recording applications [7], magnetic refrigeration [8], catalysis [9], ion recovery [10], magnetic membranes [11], gas detectors [12], bacterial reagents [13, 14], treatment of water from microbial contamination [15, 16].

There are many physical and chemical methods which are implied in NPs synthesis. The two methods are expensive and use special equipment that require high energy and involve hazardous, corrosive and flammable chemicals materials [17]. Moreover, using the above-mentioned methods are likely to arise conglomerates that reduce the surface reactivity and instability of these particles [18]. Also, the sizes, morphologies, shapes, compositions and crystallinity of nano materials, are depend on the used techniques, which highly affect the products properties. The cited methods suffer from an inability to control NPs size. Composition and size control need other methods such as green one. ... It is worth noting that green synthesis is adopted for this purpose due to greater stability of the products and their low costs without toxicity. Stability of the products refers to phytochemical compounds from food sources such as peel [19], fruits [20], and seeds [21]. Palm leaves (*Phoenix dactylifera* L.) are few used to

* Corresponding author: benhaouab@yahoo.fr

synthesis NPs [22]. Iron oxide NPs greenly synthesized using different extract become today as attractive field for researchers [23]. Even though green synthesis of iron nanoparticles has emerged using different parts of the plant and herbal materials (such as stems, roots, leaves, and seeds), which are a simple, low cost, more safety, and environmentally friendly compared to the previous cited methods [24]. The metal oxides morphology can be affected by several factors, including: the effect of the ratio between the plant extract and the precursor [22], the effect of extract plant [25], the effect of precursor concentration [26], the effect of precursor type [27], the effect of the solvent [28], the effect of the reaction time [29], the effect of the temperature of the reaction [30], the effect of pH [31], the effect of the annealing time [32], the effect of the annealing temperature [33].

The aim of this work is to study the physical properties of iron oxide nanoparticles greenly synthesized by reacting the ethanolic extract of *Phoenix dactylifera*. L with different iron chloride ($FeCl_3$) salt concentration in aqueous solution. The effect of $FeCl_3$ salt concentration within the extract and the 500°C annealed products for one hour, will be analysed using XRD, UV–VIS, SEM and FTIR.

2. Experimental details

2.1. Preparing and extracting plant materials

Palm leaves (*Phoenix dactylifera*. L) were collected from local farms in El Oued province, Algeria. Firstly, they are washed several times with tap water and distilled water to remove dust, dirt and impurities suspended to them. The palm leaves are cut into medium pieces and dried at room temperature for 10 days, then grinded to get the palm leaves sheet powder. Extraction operation palm leaves was proceed to have leaves extract by placing 50g of the previous powder with 300ml of ethanol in a 1000ml glass jar with continuous stirring for a full day at room temperature. Finally, this mixture is filtered and considered as liquid ethanolic leaves extract (L.E.L.E) mother sources for use.

2.2. Preparation of iron oxide nanoparticles

For each experimentation, iron oxides NPs are synthesized by mixing 40ml of the (L.E.L.E) with 80ml $FeCl_3$ aqueous solution at known concentrations (0.01, 0.02, 0.03, and 0.04M). The mixture has obeying to continuous stirring, in a water bath system at 70°C, for one hour. Iron oxides particles formation starts when the change in the color of the mixture, from green to dark brown, appears. After that, the blend was dried and the residual products was washed several times with double distilled water and collected by centrifugation. The collected product was dried again at 90-100°C inside the drying oven. Then the dried product was obeying to a second annealing treatment at 500°C for an hour. Photos of the prepared powders of iron oxides NPs for different $FeCl_3$ concentrations are shown in Fig. 1.

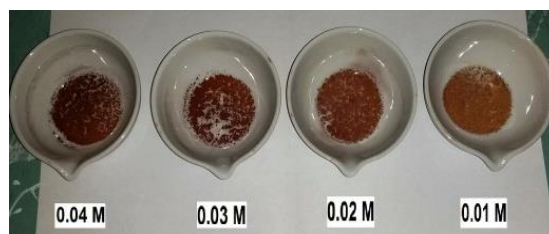


Fig. 1. Photos of the prepared powders for $FeCl_3$ concentrations.

2.3. Characterization of iron oxides nanoparticles

The band gap energy has been estimated through the optical transmittance spectrum using (UV–VIS spectrophotometer Shimadzu, Model 1800) operating in the wavelength 200-900nm range. To find out iron oxides crystal structure XRD technique was employed using X-ray diffractometer (Rigaku Miniflex 600) apparatus with a $Cu-K\alpha$ ($\lambda = 1.5406 \text{ \AA}$) operating in the 2 θ

angles of 10° to 90° range, and (30keV, 30mA) as conditions of X-ray generation. Chemical bonds of iron oxides NPs were determined by their vibration in 400-4000cm⁻¹ infrared spectrum which was scanned by a device (Nicolet iS5, Thermo Fisher Scientific). The surface investigation was done with scanning electron microscope (SEM-TESCAN VEGA 3), all measurements are done at room temperature.

3. Results and discussion

3.1. Structural properties

Fig. 2 The XRD patterns of powders treated for 1h at 500°C are shown in Fig.2. XRD peaks show the existence of three iron oxide essentials compounds:

- Gamma phase, maghemite (γ -Fe₂O₃) having a tetragonal crystalline structure according to JCPDS No: 00-025-1402 where peaks appear at 2θ : 30°.214, 35°.683, 57°.307, and 62°.885 correspond to lattice plane of (206), (119), (1115) and (4012), respectively;
- Alpha phase, hematite (α -Fe₂O₃) having a rhombohedral crystalline structure JCPDS No: 01-089-0598 where peaks appear at 2θ : 33°.130, 35°.683, 40°.951, 49°.405 and 64°.003 correspond to lattice plane of (104), (110), (113), (024) and (300), respectively;
- Beta phase, β -Fe₂O₃ having a cubic crystalline structure according to JCPDS No: 00-039-0238 appears peaks at 2θ : 33°.082, 38°.296, 55°.129, and 65°.945 correspond to lattice plane of (222), (400), (440) and (622), respectively. It is worth noting that for XRD reflection at 38.871° which is related to gamma phase is excluded because of its considerable shift.

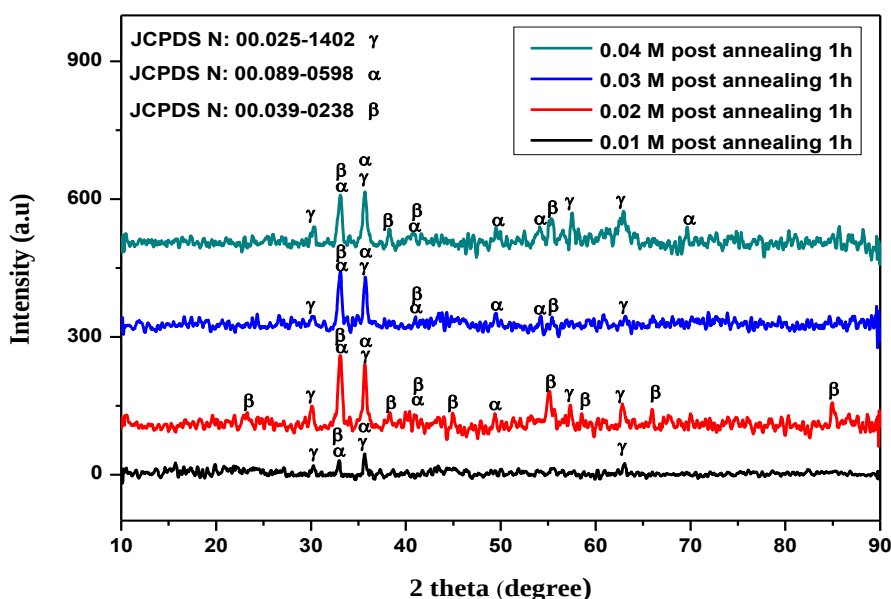


Fig. 2. X-ray diffraction patterns of samples 0.01, 0.02, 0.03 and 0.04M. (γ : γ -Fe₂O₃, α : α -Fe₂O₃, β : β -Fe₂O₃).

The lattices constant (a and c), for the tetragonal phase structure, are determined by the relations [34]:

$$2d_{hkl} \sin(\theta) = n\lambda \quad (1)$$

and

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

where ' d_{hkl} ' and ' (hkl) ' are the inter-planer distance and Miller indices, respectively. The values of lattice parameter ' a ' and ' c ' are listed in Table 1. Values of a and c are ($a = b = 8.3383\text{\AA}$, $c = 25.0151\text{\AA}$) for instance in the case of 0.04M sample; they are the most close to the values of standard JCPDS data card, ($a_0 = b_0 = 8.3400\text{\AA}$, $c_0 = 25.0200\text{\AA}$).

The lattice constants (a and c), for the rhombohedral phase structure, are determined by the relations [35]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3a^2} (h^2 + k^2 + hk) + \frac{l^2}{c^2} \quad (3)$$

The values of lattice parameter ' a ' and ' c ' are illustrated in Table 1. Values of a and c are ($a = b = 5.0339\text{\AA}$ and $c = 13.7892\text{\AA}$) in the case of 0.03M sample; they are the most close to the values of standard JCPDS ($a_0 = b_0 = 5.0380\text{\AA}$ and $c_0 = 13.7760\text{\AA}$).

For the beta phase structure, the lattice constant a is determined by the following relations of cubic unit [36]:

$$\frac{1}{d_{hkl}^2} = \frac{1}{a^2} (h^2 + k^2 + l^2) \quad (4)$$

Values of a , are illustrated in Table 1. In the case of 0.01M sample, a is about $9.4022\text{\AA}$ which is closely equal to $9.4040\text{\AA}$ of the JCPDS No: 00-039-0238 one.

The crystalline sizes of the powders, with different concentrations, are given in Table 1, they are calculated using Scherrer's formula [37]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (5)$$

where D , β , λ , and θ are the crystallite size, the full width at half-maximum (FWHM) of diffraction peaks, the X-ray wavelength ($1.5406\text{\AA}$) and Bragg angle, respectively. For gamma and beta Fe_2O_3 phases the most intense diffraction peaks are only taken in consideration which are (119) and (222), respectively. Whereas for alpha phase the crystallite size averages were taken with the help of the two peaks (104) and (110). The calculated crystallite sizes from the considered peaks are listed in Table 1. For more focus on the effect of concentration on the grain size of the products, it was remarked that the later has the same effect on all phases grain size variation as exhibited in Fig.3.

Table 1. Crystallographic data obtained from XRD.

Sample	Phases present	Grain size (nm)	Calculated d ($\text{\AA}$)	Standard d ($\text{\AA}$)	Lattice parameter a ($\text{\AA}$), b ($\text{\AA}$), c ($\text{\AA}$)
0.01 M	$\gamma\text{-Fe}_2\text{O}_3$	37.39043	2.51576	2.51400	$a = b = 8.3438$, $c = 25.0314$
	$\alpha\text{-Fe}_2\text{O}_3$	31.32887	2.71418	2.70329	$a = b = 5.0315$, $c = 13.8775$
	$\beta\text{-Fe}_2\text{O}_3$	25.25763	2.71418	2.71400	$a = 9.4022$
0.02 M	$\gamma\text{-Fe}_2\text{O}_3$	25.94565	2.51383	2.51400	$a = b = 8.3374$, $c = 25.0123$
	$\alpha\text{-Fe}_2\text{O}_3$	22.24205	2.70650	2.70329	$a = b = 5.0361$, $c = 13.8101$
	$\beta\text{-Fe}_2\text{O}_3$	18.54299	2.70650	2.71400	$a = 9.3756$
0.03 M	$\gamma\text{-Fe}_2\text{O}_3$	22.91024	2.51698	2.51400	$a = b = 8.3374$, $c = 24.9904$
	$\alpha\text{-Fe}_2\text{O}_3$	20.43640	2.70409	2.70329	$a = b = 5.0339$, $c = 13.7892$
	$\beta\text{-Fe}_2\text{O}_3$	17.96256	2.70409	2.71400	$a = 9.3671$
0.04 M	$\gamma\text{-Fe}_2\text{O}_3$	34.36907	2.51679	2.51400	$a = b = 8.3383$, $c = 25.0151$
	$\alpha\text{-Fe}_2\text{O}_3$	26.89509	2.70397	2.70329	$a = b = 5.0336$, $c = 13.7892$
	$\beta\text{-Fe}_2\text{O}_3$	19.42119	2.70397	2.71400	$a = 9.3668$

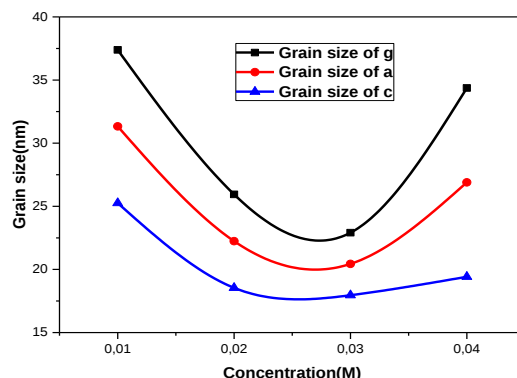


Fig. 3. Grain size with various concentration (γ : γ - Fe_2O_3 , α : α - Fe_2O_3 , β : β - Fe_2O_3).

3.2. Surface morphology

The surface morphology of iron oxide powders are studied using SEM images, for different magnification $5\mu\text{m}$ for the first concentration and $1\mu\text{m}$ for the rest, Fig. 4a-d shows the results with different concentration of FeCl_3 : 0.01, 0.02, 0.03 and 0.04 M, respectively. It is clear that iron oxides NPs are mainly present as granules with spherical shaped particles. The agglomeration of particles behaves as in the case of XRD. They begun with spherical shaped particles of about $1.2\mu\text{m}$ then decreases to 0.8 - $0.5\mu\text{m}$ for concentration of 0.02, 0.03 M and increases to attain $1\mu\text{m}$ for the concentration of 0.04 M. To have idea about the composition of NPs, EDAX for one sample is reported in this study; it reveals that the samples are composed of iron and oxygen in atomic ratio of 2, as shown in the EDAX table below (Fig. 4e), which means a non stoichiometric composition of the elaborated iron oxides NPs. As it was shown from the XRD study that the co-existence of three types of iron oxides NPs which are γ , α and β - Fe_2O_3 and the same behaving of the grain size (XRD) and the agglomeration under its spherical shaped particles (MEB) within the FeCl_3 concentration; it may be proclaimed that the co-existence of the three species was at the origin of the spherical shapes.

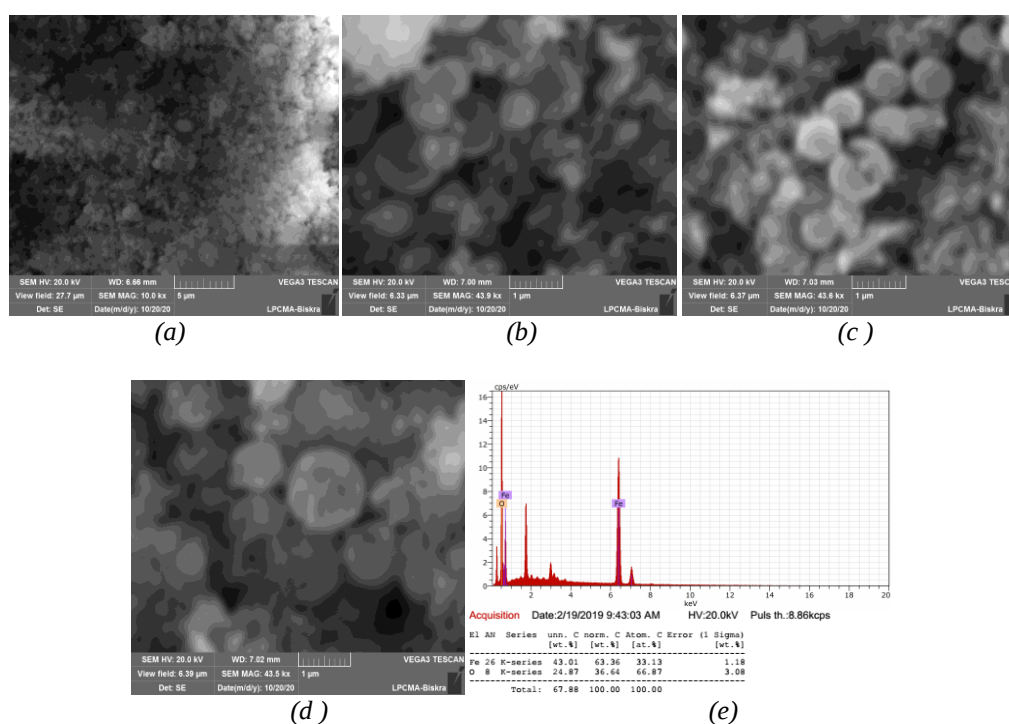


Fig. 4: Scanning electron microscopic images of iron oxide NPs powders: (a) 0.01, (b) 0.02, (c) 0.03 and (d) 0.04 M., (e) EDAX of arbitrary chosen sample.

3.3. Optical properties

In order to investigate the band gap of the iron oxide NPs powders, Tauc's relation is used [38]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (6)$$

where α , h , ν , and E_g are the absorption parameter, Planck constant, the photon frequency and gap energy, respectively; A is a constant and n is taken 1/2 based on consideration that γ -Fe₂O₃ and α -Fe₂O₃ have direct gap [38, 39]. The optical absorption data was used to generate plots of $(\alpha h\nu)^2$ vs $h\nu$, as shown in Fig.5. leading to band gap energy which was estimated by extrapolating the straight line of $(\alpha h\nu)^2$ to $h\nu$ axis. Optical values of the elaborated samples are given in Table 2. As shown leading to band gap energy of 2.162 , 2.295, 2.358, and 2.218eV for concentrations 0.01, 0.02, 0.03, and 0.04M, respectively. Those values are in agreement with several previous works [39-42].

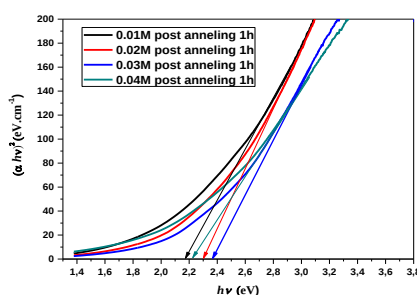


Fig. 5. Band gap (E_g) estimation from Tauc's relation for iron oxide NPs Powders.

Table 2. Optical gap of green synthesized iron oxide NPs.

Concentration (M)	Optical gap E_g (eV)
0.01	2.162
0.02	2.295
0.03	2.358
0.04	2.218

3.4. FTIR

Fig.6 shows FTIR spectrum of the synthesized samples with different precursor concentrations. The bands in the range of 400-900 cm⁻¹ are related to Fe-O lattice vibration. As exhibits in the figure bands at 562, 633 and 692 cm⁻¹ are related at maghemite phase formation whereas bands at 542, 573cm⁻¹ describes the formation of hematite phase [43] and band 528cm⁻¹ is related at beta phase [44]. The peak 800 cm⁻¹ is related to O-H out of plane bond [43].

Absorption peaks at 1106 and 3420 cm⁻¹ also appeared, may be they assigned to C-O vibration mode [45], and to O-H stretching vibration [46].

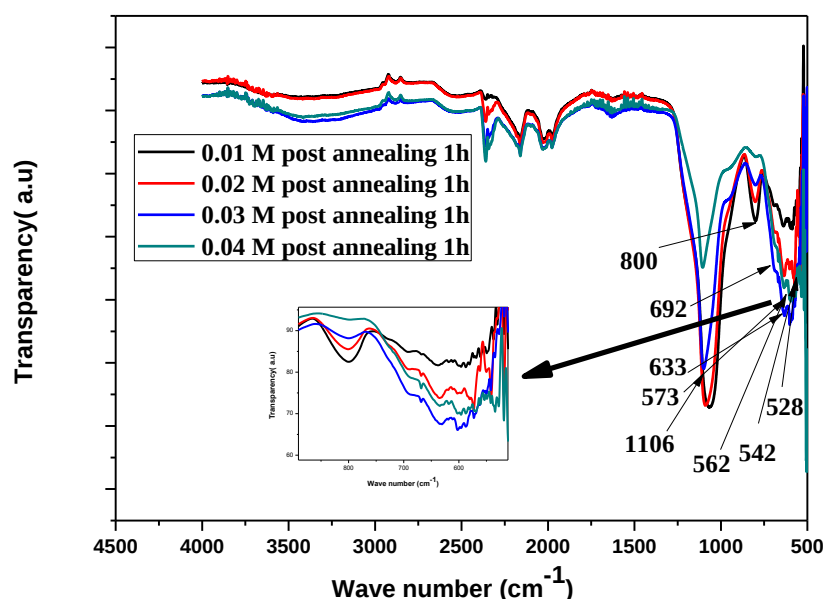


Fig. 6. FTIR spectrum of iron oxides NP powders for (0.01-0.04M) post annealing at 500°C.

4. Conclusion

In this work, Iron oxide NPs powders were synthesized by green synthesis method using the extract of *Phoenix dactylifera* L. with a triple iron chloride solution. The effect of salt concentration in the extract for concentrations: 0.01M, 0.02M, 0.03M, and 0.04M of post heat treatment at 500°C on their structural and optical properties have been studied. XRD analyses affirmed the formation of three iron oxide NPs essential compounds: maghemite phase, hematite phase, and beta phase whereas the grain size varies upon iron chloride concentration and it was arranged in 22.91-37.40nm, 20.41-31.32nm and 17.96-25.25nm respectively. SEM images showed that all samples having spherical shaped particles. With direct band gap in the range of 2.162-2.358eV. FTIR spectrum affirms the abundance of Fe-O bond.

References

- [1] X. Zhang, S. Lin, Z. Chen, M. Megharaj, R. Naidu, *Water Research* **45**(11),3481 (2011).
- [2] S. Mornet, S. Vasseur, F. Grasset, P. Veverka, G. Goglio, A. Demourgues, J. Portier, E. Pollert, E. Duguet, *Progress in Solid State Chemistry* **34**(2-4),237 (2006).
- [3] J. Petr, B. Teste, S. Descroix, J.M. Siaugue, P. Gareil, A. Varenne, *Electrophoresis* **31**(16), 2754 (2010).
- [4] H. Parrot-Lopez, F. Perret, B. Bertino-Ghera, *Annales pharmaceutiques françaises* **68**, 12(2010).
- [5] S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. Vander Elst, R.N. Muller, *Chemical reviews* **108**(6),2064 (2008).
- [6] K.-J. Lee, J.-H. An, J.-S. Shin, D.-H. Kim, C. Kim, H. Ozaki, J.-G. Koh, *Nanotechnology* **18**(46),465201 (2007).
- [7] R.J. Veitch, *IEEE transactions on magnetics* **37**(4),1609 (2001).
- [8] G. Bisio, G. Rubatto, P. Schiapparelli, *Energy conversion and management* **40**(12), 1267 (1999).
- [9] M.-H. Liao, D.-H. Chen, *Journal of Molecular Catalysis B: Enzymatic* **18**(1-3),81 (2002).
- [10] M. Takafuji, S. Ide, H. Ihara, Z. Xu, *Chemistry of materials* **16**(10),1977 (2004).
- [11] E. Sourty, D. Ryan, R. Marchessault, *Cellulose* **5**(1),5 (1998).
- [12] K. Šíroky, J. Jirešová, L. Hudec, *Thin Solid Films* **245**(1-2),211 (1994).

- [13] M. Arakha, S. Pal, D. Samantarrai, T.K. Panigrahi, B.C. Mallick, K. Pramanik, B. Mallick, S. Jha, *Scientific reports* **5**(1),1 (2015).
- [14] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X. Xie, *Science of the Total Environment* **424**(1),1 (2012).
- [15] K. Al-Saad, M. Amr, D. Hadi, R. Arar, M. Al-Sulaiti, T. Abdulmalik, N. Alsahamary, J. Kwak, *Arab Journal of Nuclear Sciences and Applications* **45**(2),335 (2012).
- [16] W. Yan, A.A. Herzing, C.J. Kiely, W.-x. Zhang, *Journal of Contaminant Hydrology* **118**(3-4), (2010).
- [17] T. Shahwan, S.A. Sirriah, M. Nairat, E. Boyacı, A.E. Eroğlu, T.B. Scott, K.R. Hallam, *Chemical Engineering Journal* **172**(1),258 (2011).
- [18] D. O'Carroll, B. Sleep, M. Krol, H. Boparai, C. Kocur, *Advances in Water Resources* **51**(1), 104 (2013).
- [19] Y. Wei, Z. Fang, L. Zheng, L. Tan, E.P. Tsang, *Materials Letters* **185**(1),384 (2016).
- [20] E. Rostamizadeh, A. Iranbakhsh, A. Majd, S. Arbabian, I. Mehregan, *Journal of Nanostructure in Chemistry*, 1 (2020).
- [21] R. Rahmani, M. Gharanfoli, M. Gholamin, M. Darroudi, J. Chamani, K. Sadri, *Journal of Molecular Structure* **1196**(1),394 (2019).
- [22] D. Berra, S. Laouini, B. Benhaoua, M. Ouahrani, D. Berrani, A. Rahal, *Digest Journal of Nanomaterials and Biostructures* **13**(4),1231 (2018).
- [23] A. Bouafia, S.E. Laouini, A. Khelef, M.L. Tedjani, F. Guemari, *Journal of Cluster Science*, 1 (2020).
- [24] K.M. Kumar, B.K. Mandal, K.S. Kumar, P.S. Reddy, B. Sreedhar, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **102**(1),128 (2013).
- [25] N.Y. Stozhko, M.A. Bukharinova, E.I. Khamzina, A.V. Tarasov, M.B. Vidrevich, K. Z. Brainina, *Nanomaterials* **9**(12),1655 (2019).
- [26] R.B. Ayed, M. Ajili, N.K. Turki, *Physica B: Condensed Matter* **563**(1),30 (2019).
- [27] X. Qin, Y. Ju, S. Bernhard, N. Yao, *Journal of materials research* **20**(11),2960 (2005).
- [28] A.U. Limaye, J.J. Helble, *Journal of the American Ceramic Society* **86**(2),273 (2003).
- [29] V. Karade, T. Dongale, S.C. Sahoo, P. Kollu, A. Chougale, P. Patil, P. Patil, *Journal of Physics and Chemistry of Solids* **120**(1),161 (2018).
- [30] A. Samy, A.E. El-Sherbiny, A. Menazea, *Egyptian Journal of Chemistry* **62**,29 (2019).
- [31] M.S.F.A. Zamri, N. Sapawe, *Materials Today: Proceedings* **19**(1),1321 (2019).
- [32] A. Jafari, S.F. Shayesteh, M. Salouti, K. Boustani, *Journal of Magnetism and Magnetic Materials* **379**(1),305 (2015).
- [33] T.M. Laid, K. Abdelhamid, L.S. Eddine, B. Abderrhmane, *Journal of Molecular Structure* **1229**(1),129497 (2021).
- [34] C. Kittel, P. McEuen, P. McEuen, Wiley New York, 1996.
- [35] L. Dghoughi, B. Elidrissi, C. Bernede, M. Addou, M.A. Lamrani, M. Regragui, H. Erguig, *Applied Surface Science* **253**(4),1823 (2006).
- [36] A. Sadanandan, M.J. Mathew, *AIP Conference Proceedings*, AIP Publishing LLC, **1**, 20157(2019).
- [37] M. Abdullah, K. Khairurrijal, *Jurnal Nanosains & Nanoteknologi* **1**(1),28 (2009).
- [38] J. Tauc, R. Grigorovici, A. Vancu, *physica status solidi B* **15**(2),627 (1966).
- [39] P. Mallick, B. Dash, *Nanosci. Nanotechnol.* **3**(5),130 (2013).
- [40] R.N. Goyal, D. Kaur, A.K. Pandey, *Materials Chemistry and Physics* **116**(2-3),638 (2009).
- [41] J. Liu, H. Yang, X. Xue, *Materials Letters* **229**,156 (2018).
- [42] Z. Wei, X. Wei, S. Wang, D. He, *Materials Letters* **118**,107 (2014).
- [43] M. Ates, I.C. Cimen, I. Unal, B. Kutlu, B. Ertit Tastan, D. Danabas, O. Aksu, Z. Arslan, *Environmental toxicology* **35**(3),385 (2020).
- [44] W.J. Aziz, M.A. Abid, D.A. Kadhim, M.K. Mejbel, *Materials Science and Engineering IOP Publishing* **881**(1),12099(2020).
- [45] A.T. Khalil, M. Ovais, I. Ullah, M. Ali, Z.K. Shinwari, M. Maaza, *Green Chemistry Letters and Reviews* **10**(4),186 (2017).
- [46] J. Ding, Q. Zhong, S. Zhang, *Journal of Molecular Catalysis A: Chemical* **393**,222 (2014).